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ATMOSPHERIC CHEMISTRY

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Lecture 1: The Present Atmosphere

1.1 Introduction

The chemical composition of the terrestrial atmosphere differs markedly from those of its immediate neighbours in the Solar System. Mars and Venus have atmospheres which are composed almost entirely (in excess of 95%) of carbon dioxide with exceedingly small concentrations of molecular oxygen and water vapour. By contrast, the terrestrial atmosphere contains large amounts of molecular oxygen (21%) and carbon dioxide (though still important) is present only in small quantities. Not only is the terrestrial different, it is substantially displaced from chemical equilibrium. The extent to which selected compounds depart from equilibrium is illustrated in Table 1.

Molecule	Equilibrium Concentration	Present Concentration	Residence Time
N_2	$<10^{-10}$	0.78	1.6×10^{7} yr
CH_4	$<10^{-35}$	1.7×10^{-6}	6 yr
N_2O	$<10^{-20}$	3×10^{-7}	20 yr
NH_3	$<10^{-35}$	10^{-9}	10 days
H_2	$<10^{-35}$	5×10^{-7}	4 yr

Table 1 Actual and equilibrium concentrations of selected constituent in the terrestrial atmosphere assuming present day O_2.

Estimates of residence times for the different species vary over wide limits (column 3). The N_2 residence time is comparable with geological timescales. Others are much shorter (days). The composition of the Earth's atmosphere is thus maintained in a steady state disequilibrium.

In these lectures the physical, biological and geochemical processes which produced and maintain the concentrations of the major constituents will be described. The shorter timescale processes which determine the concentrations of trace gases such as ozone will be presented and the extent to which man's activities are perturbing the system will be discussed.

1.2 Structure of the Present Atmosphere

The thermal structure and principal motion fields in the atmosphere are strong functions of the strengths of the radiative sources and sinks in the atmosphere and hence of the chemical composition and cloud cover. A representation of the thermal structure of the globally averaged atmosphere is shown in Figure 1. The atmosphere can be usefully divided into regions on the basis of the vertical temperature gradient dT/dz. It can be inferred that the troposphere is heated from below while the stratosphere is heated from above. In consequence, the stratosphere has timescales for vertical exchange which are long, while the troposphere has short exchange times. The temperature falls again above the stratopause (the mesosphere), and rises in the thermosphere. In the region below ≈100 km the mean molecular weight (mainly determined by N_2

and O_2) varies little. This region, that of our principal concern, is termed the homosphere.

1.3 Solar Radiation

The sun emits radiation approximately corresponding to a black body at between 5800K and 6000K, with peak energies in the visible at wavelengths between 0.4μm and 0.6μm (400-600nm). By contrast the earth's atmosphere emits radiation approximately characteristic of a black body at 255K, with peak energies in the infra-red at wavelengths of ≈15μm (15000nm). The fact that the black body curves at 6000K and 255K do not overlap significantly (Figure 2a)) allows the incoming solar and outgoing terrestrial radiation fluxes to be treated almost independently when computing the heat balance. Shown in Figure 2b) is the atmospheric attenuation, which is due to the combined absorptions of a large number of gases. One characteristic of the atmospheric absorption is that high energy UV radiation at wavelengths shorter than ≈300nm is absorbed in the upper atmosphere by molecular oxygen and ozone and does not reach the surface. The second important characteristic is that atmospheric absorption is high in the region of the outgoing terrestrial radiation flux. It is this absorption of outgoing radiation by what are popularly termed 'greenhouse gases' which raises the surface temperature by 20-30K over that of an atmosphere free planet. It can be seen that in the infra-red, neither of the main atmospheric constituents (N_2 or O_2) possess absorption features. This arises because both molecules are diatomic and homonuclear - their symmetry implies that neither possess

electromagnetic dipole moments for vibration/rotation transitions in the infra-red. In fact, at high pressures (in this case appropriate to the low stratosphere), oxygen molecules can, on collision with either O_2 or N_2, become sufficiently deformed to possess momentarily a dipole moment. This results in a weak but detectable diffuse pressure induced O_2 absorption band in the mid infra-red at about 6μm (6000nm).

The molecules primarily responsible for absorbing radiation in the earth's atmosphere are O_2, O_3 (ozone), H_2O and CO_2. In Figure 3 are shown the contributions of the gases to the net radiative heating and cooling at different levels in the atmosphere. Absorption of solar radiation by O_2 and O_3 are respectively responsible for strong radiative heating in the thermosphere and around the stratopause. The mechanism for this heating is firstly the absorption of a solar photon (denoted here by hv where h is Planck's constant and v the frequency) which induces dissociation viz:

$$O_2 + hv \rightarrow O + O$$

or $$O_3 + hv \rightarrow O_2 + O$$

followed by recombination

$$O + O_2 + M \rightarrow O_3 + M^*$$

which in effect converts the photon energy to translational (heat) energy. M is any molecule, the * denoting excitation. The recombination reaction occurs fast everywhere except in the thermosphere where the long lifetime of atomic oxygen results in significant heat transport. In some instances de-excitation by collision may occur before dissociation with the same net effect.

In the stratosphere, the absorption of solar radiation is partially balanced by infra-red cooling due to CO_2 and to a lesser extent O_3. In

the troposphere radiative cooling is mainly due to H_2O (the H_2O cooling is partially offset by absorption of solar radiation in the near infra-red). By comparison, the effects of CO_2 are computed to be small. The net radiative cooling in the troposphere of ≃1K/day is balanced by the transfer of sensible and latent heat from the surface. The low stratosphere shows a small net heating (energy emitted from the warm troposphere) while the middle stratosphere is very close to radiative equilibrium. The upper stratosphere and mesosphere on the other hand shows a net heating rate of ≃2K/day, arising from O_3 absorption. Absorption by O_2 is chiefly responsible for the net heating in the lower thermosphere. The figures presented above are for a globally averaged case. Examination of the latitude distribution of the heating rates shows (e.g. London) that for example in solstice conditions, the net heating in the high latitude summer stratosphere and mesosphere exceeds 5-10K/day with a corresponding cooling in the winter hemisphere. It is this latitude gradient in heating rate which is so important in the circulation of the upper atmosphere.

Ozone thus shields the troposphere from harmful solar UV radiation and heats the stratosphere, while at the same time attenuating the outgoing infra-red flux. CO_2 increases will warm the troposphere and surface; and cool the stratosphere. H_2O increases will warm the troposphere directly, but may also affect the radiative balance indirectly by influencing ozone photochemistry or cloud properties and amounts. Cloud effects are hard to chracterise as they effect both the incoming solar and outgoing terrestrial radiation fluxes.

1.4 The Atmospheric Window

As has been stated above, in the absence of clouds, O_3, H_2O and CO_2 are responsible for most atmospheric absorption in the infra-red. However, close inspection of the absorption properties of these gases (Figure 4) shows that there are region in the infra-red where the net atmospheric absorption is weak. The main region of low absorption (8 - 12 μm, 8000-12000nm), in the middle of which a strong atmospheric ozone band resides, has a net atmospheric transmission of ≈90% i.e. 90% of the radiation emitted from the surface will reach space, and is thus termed an atmospheric 'window'. This region is important radiatively as it encompasses a significant portion of the terrestrial radiation emission curve (Figure 2a)). Atmospheric gases with absorption bands in this window region would be effective attenuators of outgoing terrestrial radiation and thus as greenhouse gases because

1) their absorptions would be close to the peak energy of the outgoing radiation flux,

and 2) because the atmospheric transmission is high (the same absorption in regions of low transmission would have proportionally smaller effects).

In Figure 5 are shown molecules which are known to possess absorption bands in the window region. The ordinate has no significance. The presence in the atmosphere of many of the molecules identified in this Figure can be related directly to man's activities. The concentrations of others, a notable example being O_3, are determined by

complex photochemical balances involving the emission and subsequent breakdown of molecules arising naturally and from man's activities.

1.5 Trace Gases and Climate

There is no formal definition of what constitutes a trace gas. The usual loose definition is that trace gases are those present in the atmosphere at up to ≈10ppmv (parts per million by volume). CO_2 is present in the atmosphere at mixing ratios of ≈340 ppmv (parts per million by volume) and so by this definition is not a trace gas. However, it is important to include it in any discussion because it is the single most important greenhouse gas and serves as a useful reference point. Also, although CO_2 is not photochemically active it has an important influence on the trace greenhouse gas O_3 through temperature dependences in the ozone photochemistry.

An obvious question is whether gases present at mixing ratios of only ppbv (parts per billion by volume) can have effects significant compared to CO_2. The answer is yes: much of the CO_2 absorption bands have very high absorptions and so essentially zero transmission. Even a major increase in absorption cannot therefore affect the transmission further. In contrast, those of many trace gases are in the high transmission window region and are optically thin. For example one molecule of F-12, a commonly used refrigerant, is as effective radiatively as 10^4 molecules of CO_2. Other gases absorbing in the window region are similarly effective. Many trace gases are also known to be important in the photochemistry of ozone. This can lead to changes in

O_3 concentrations which then could then conceivably effect the radiation balance.

1.5.1 Trends in Radiatively Active Trace Gases

Many trace gases have lifetimes in the atmosphere comparable to or greater than the tropospheric interhemispheric mixing time (approximately 1 year). In these cases spatial gradients in their tropospheric mixing ratios will be small. In these circumstances it is possible to detect atmospheric composition changes using a single observing station. For example, in Figure 6 are shown CO_2 mixing ratios measured at Mauna Loa Observatory in the central Pacific. Two features are apparent

1) there is a strong annual signal associated with the seasonal cycle of vegetation respiration, and

2) there is a continuous upward trend in mixing ratio at a rate of ≈0.4% per year in recent years.

There are observations from other stations which show annual cycles with phasing appropriate to their locations, but with the same overall trend. The trend is largely caused by increased fossil fuel burning.

Nitrous oxide (N_2O), the source of stratospheric reactive nitrogen oxides, is observed to be increasing at ≈0.2%/year (Figure 7). This rate of increase implies a 30% discrepancy between the suppposed sources (combustion, aerobic microbial activity, soil emissions) and the known sink (photolysis in the stratosphere).

Methane (CH_4), a gas which plays a very complicated role in tropospheric and stratospheric photochemistry, is known to be increasing

at on average 1%/year (Figure 8). This increase consists of periods of more rapid growth (≈1.8%/year) interspersed with periods of decline, the most recent being contemporaneous with the recent El Nino event in 1982-3. Analysis of air trapped in polar ice show that methane mixing ratios have been increasing for several centuries, and have roughly doubled from values of ≈0.7ppmv that prevailed for thousands of years prior to the recent increase. Uncertainties surrounding increases in methane are a particular cause of concern. Methane is destroyed mainly in the troposphere (where the relatively rapid mixing still ensures an essentially uniform distibution) by reaction with the hydroxyl radical OH (the sink mechanism of many species - see Table 2). While sources of methane have been identified (termites, enteric fermentation in ruminants (mainly cattle) and rice paddies), there remains great uncertainty regarding their magnitudes. The result is that the doubling in methane over the last several hundred years is not understood. Any extrapolation of methane mixing ratios into the future would be heavily dependent on assumptions concerning future OH concentrations. This in turn would depend on H_2O concentrations and hence on any global warming. Since methane and CO are the dominant consumers of tropospheric OH (and vice-versa), it is possible that there are feedback effects e.g.

more CH_4 → less OH → more CH_4 → less OH etc.

One model showed that only a 65% increase in the methane sources would double atmospheric methane mixing ratios. The resulting decrease in OH could significantly lengthen the atmospheric lifetimes of many species (Table 2) possibly increasing penetration of these gases from the troposphere into the stratosphere. Nor is the problem simply one of OH and methane (or CO). The emission rates of nitrogen oxides would also

influence future OH concentrations, via in this case changes in the tropospheric ozone production cycle (see lecture 6).

The relatively short atmospheric lifetime of CO leads to significant atmospheric variability and a pronounced interhemispheric gradient which in turn makes estimating trends in CO concentrations highly uncertain. However, recent measurements at several locations suggest an annual rate of increase of around 2%/year over the period 1951-81 and an increase of around 5%/year 1979-82 - largely anthropogenic. Increases in CO would further reduce tropospheric OH concentrations and increase tropospheric lifetimes of many molecules for the reasons outlined above.

In Figure 10 are shown time series of the surface concentrations of the major chloro-fluoro-carbons, F-11 ($CFCl_3$) and F-12 (CF_2Cl_2). These gases have found widespread industrial use because of their chemical inertness in the troposphere. However, once they permeate into the upper atmosphere, they are no longer shielded from short wavelength solar UV radiation and they are photodissociated at those levels where the released chlorine can actively participate in photochemical ozone destruction. Production of these two CFCs has (excluding the USSR) increased rapidly since their introduction in the 1930s, increasing to a maximum in the mid 1970s, with a small decline to the mid 1980s and a subsequent increase since then. Production in the USSR is currently estimated to contribute 20-30% to the total and is on the increase. Clear upward trends are apparent in F-11 and F-12 concentrations, of around 5% per year. Other halogens such as methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4) show rates of increase in the troposphere of between 4-8%/year and 0.5-1.5%/year respectively. Methyl chloride (CH_3Cl) is the major natural contributor to the atmospheric

chlorine budget, with industry estimated to add ≈25%. To put these changes in perspective, atmospheric chlorine has essentially doubled over the last two decades due to man's activities, compared to an estimated increase in nitrous oxide of less than 5% over the same period.

Anthropogenic bromine compounds have also been observed in the atmosphere. Once released, bromine is particularly effective in the photochemical destruction of ozone. A gas of particular importance both as a greenhouse gas and photochemically (as the source of OH) is H_2O. However, uncertainties surrounding the mechanism(s) which restrict its passage into the stratosphere mean that the prediction of trends in stratospheric H_2O is highly uncertain. The solution adopted in most models is to adopt a constant stratospheric H_2O injection mixing ratio. Changes in tropospheric H_2O concentrations are likely to be linked to climate change.

1.6 Radiative Effects

As already indicated, all the above mentioned gases are potentially important greenhouse gases (absorption bands in the 8-12μm (8000-12000nm) region of the electromagnetic spectrum). Most also have a photochemical effect on the distribution of atmospheric ozone (and thence on radiation). The relative effectiveness of a number of greenhouse gases in changing the surface temperature is shown in Figure 11 (note the logarithmic temperature scale). These are results from a 1 dimensional (height) global average radiative convective model (RCM). The relative effectiveness of the CFCs relative to tropospheric O_3, CH_4

and N_2O is demonstrated by the fact that the last three species are 2-3 orders of magnitude more plentiful, yet with comparable impact on the surface temperature.

Taking estimates of the rates of increase of various gases which are active radiatively or chemically (or both) (see Table 2), it is possible to predict future surface warmings. In Figure 12 is shown the surface warming over the period 1980-2030 predicted using a 1 d RCM model with the composition changes shown in Table 2. These calculations do not include explicitly the effects of changes in cloud cover or cloud optical properties nor, obviously, can they reflect any regional differences or take account of other influences like long term changes in sea surface temperatures. However, despite these limitations, at least in this model the *relative* effect of trace gases is seen to be comparable to that of CO_2 alone, expanding greatly the scope of the climate change problem. The modelled changes in ozone are particularly uncertain. A decrease in stratospheric ozone, irrespective of altitude, would lead to an increase in the downward solar UV flux reaching the surface and would thus lead to a surface warming. However, ozone is also optically active in the infra-red (at 9.6μm, 9600nm - see Figure 4). A reduction in stratospheric ozone would also lead to a stratospheric cooling, which in turn would reduce the downward flux and hence cool the troposphere and surface. However, the net infra-red absorption of CO_2, O_3 and H_2O is sufficiently strong that any cooling would diminish as the altitude of the depletion rises- the net effect of O_3 is thus critically dependent on the altitude distribution of any O_3 change. It is not clear that models can accurately predict this.

Chemical Group	Chemical Formula	Dominant Source*	Dominant Sink*	Estimated Average Residence Time (τ_i), years	Year 1980 Global Average Mixing Ratio, ppbv†	Year 2030 Probable Global Average Concentration, ppb		Remarks (also see text for details)
						Best Estimate	Possible Range	
Carbon dioxide	CO_2	N,A	O	2	339×10^3	450×10^3		Based on a 2.4% increase over the next 50 years
Nitrogen compounds	N_2O	N,A	S(UV)	120	300	375	350–450	Combustion and fertilizer sources
	NH_3	N,A	T	0.01	< 1	< 1		Concentration variable and poorly characterized
	$(NO + NO_2)$	N,A	T(OH)	0.001	0.05	0.05	0.05–0.1	Concentration variable and poorly characterized
Sulfur compounds	CSO	N,A	T(O,OH)?	1(?)	0.52	0.52		Sources and sinks largely unknown
	CS_2	N,A	T	1(?)	< 0.005	< 0.005		Sources uncharacterized
	SO_2	A(?)	T(OH)	0.001	0.1	0.1	0.1–0.2	Given the short lifetime the global presence of SO_2 is unexplained
	H_2S	N	T(OH)	0.001	< 0.05	< 0.05		
Fully fluorinated species	CF_4 (FC14)	A	I	> 500	0.07	0.24	0.2–0.31	Aluminum industry a major source
	C_2F_6 (FC116)	A	I	> 500	0.004	0.02	0.01–0.04	Aluminum industry a major source
	SF_6	A	I	> 500	0.001	0.003	0.002–0.05	
Chlorofluorocarbons	CCl_3F (F13)	A	S(UV),I	400	0.007	0.06	0.04–0.1	All chlorofluorocarbons are of exclusive man-made origin. A number
	CCl_2F_2 (F12)		S(UV)	110	0.28	1.8	0.9–3.5	of regulatory actions are pending. The nature of regulations and
	$CHClF_2$ (F22)	A	T(OH)	20	0.06	0.9	0.4–1.9	their effectiveness would greatly affect the growth of these
	CCl_3F (F11)	A	S(UV)	65	0.18	1.1	0.5–2.0	chemicals over the next 50 years.
	CF_3CF_2Cl (F115)	A	S(UV)	380	0.005	0.04	0.02–0.1	
	$CClF_2CClF_2$ (F114)	A	S(UV)	180	0.015	0.14	0.06–0.3	
	CCl_2FCClF_2 (F113)	A	S(UV)	90	0.025	0.17	0.08–0.3	
Chlorocarbons	CH_3Cl	N(O)	T(OH)	1.5	0.6	0.6	0.6–0.7	Dominant natural chlorine carrier of oceanic origin
	CH_2Cl_2	A	T(OH)	0.6	0.03	0.2	0.1–0.3	A popular reactive but nontoxic solvent
	$CHCl_3$	A	T(OH)	0.7	0.01	0.03	0.02–0.1	Used for manufacture of F22; many secondary sources also exist
	CCl_4	A	S(UV)	25–50	0.13	0.3	0.2–0.4	Used in manufacture of fluorocarbons; many other applications as well
	CH_2ClCH_2Cl	A	T(OH)	0.4	0.03	0.1	0.06–0.3	A major chemical intermediate (global production = 10 tg/yr); possibly toxic
	CH_3CCl_3	A	T(OH)	8.0	0.14	1.5	0.7–3.7	Nontoxic, largely uncontrolled degreasing solvent
	C_2HCl_3	A	T(OH)	0.02	0.005	0.01	0.005–0.02	Possibly toxic, declining markets because of substitution to CH_3CCl_3
	C_2Cl_4	A	T(OH)	0.5	0.03	0.07	0.03–0.2	Possibly toxic, moderate growth due to substitution to CH_3CCl_3
Brominated and iodated species	CH_3Br	N	T(OH)	1.7	0.01	0.01	0.01–0.02	Major natural bromine carrier
	$CBrF_3$ (F13B1)	A	S(UV)	110	0.001	0.005	0.003–0.01	Fire extinguisher
	CH_2BrCH_2Br	A	T(OH)	0.4	0.002	0.002	0.001–0.01	Major gasoline additive for lead scavenging; also a fumigant
	CH_3I	N	T(UV)	0.02	0.002	0.002		Exclusively of oceanic origin
Hydrocarbons, CO, H_2	CH_4	N	T(OH)	5–10	1650	2340	1850–3300	A trend showing increase over the last 2 years has been identified
	C_2H_6	N	T(OH)	0.3	0.8	0.8	0.8–1.2	Predominantly of auto exhaust origin
	C_2H_2	A	T(OH)	0.3	0.06	0.1	0.06–0.16	No trend has been identified to date
	C_3H_8	N,	T(OH)	0.03	0.05	0.05	0.05–0.1	No trend has been identified to date
	CO	N,A	T(OH)	0.3	90	115	90–160	No trend has been identified to date
	H_2	N,A	T(SL,OH)	2	560	760	560–1140	
Ozone	O_3 (Tropospheric)	N	T(UV, SL,O)	0.1–0.3	F(Z)‡	12.5%		A small trend appears to exist but data are insufficient
Aldehydes	$HCHO$	N	T(OH,UV)	0.001	0.2	0.2		Secondary products of hydrocarbon oxidation
	CH_3CHO	N	T(OH,UV)	0.001	0.02	0.02		1980 concentration estimated from theory

*N, natural; A, anthropogenic; O, oceanic; S, stratosphere; UV, ultraviolet photolysis; T, troposphere; OH, hydroxyl radical removal; I, ionospheric and extreme UV and electron capture removal; SL, soil sink.

†These concentrations are integrated averages; for chemicals with lifetimes of 10 years or less, significant latitudinal gradients can be expected in the troposphere; for chemicals with extremely short lifetimes (0.001–0.3 years) vertical gradients may also be encountered.

‡Varies from 25 ppbv at the surface to about 70 ppbv at 9 km. The concentration was increased uniformly by the same percentage from the surface to 9 km.

Table 2 Estimates of the abundances of trace chemicals in the global atmospheres of 1980 and 2030. Also shown are dominant sources and sinks, and estimated average atmospheric residence times.

Uncertainties in predicted surface temperature changes arise both from errors in the assumed composition growth rates and from incomplete or inaccurate knowledge of the photochemistry. For example the computed rates of ozone depletion in the low stratosphere for a given set of trace gas increases has fluctuated widely (Figure 13). The major changes have come about through modification of the rates of chemical reactions or in the coupling of different chemical species, notably chlorine and nitrogen oxides. The biggest change (in 1977) was produced by changes in hydrogen oxide chemistry, which shifted the balance of ozone destruction towards chlorine chemistry and away from nitrogen chemistry with obvious consequences.

Figure 14 shows the range of column O_3 depletion predicted by a 1 d (vertical only) model with several different trace gas growth assumptions. One run (A) with constant CFC release rates but increasing CH_4 and N_2O and CO_2 actually shows an ozone *increase*. Run B is as run A except CH_4 and N_2O held constant. Run C - as run A except CFC release increasing at 1.5%/year, and run D, which shows a very rapid ozone decline, is as run B except CFC release increasing at 3%/year (equivalent to a 20 fold increase in 100 years). If we couple into these calculations the fact that tropospheric OH concentrations are highly uncertain and possible OH trends are poorly understood; that even in the present atmosphere there are areas of significant disagreement between model and observation (the upper stratosphere); and that models have entirely failed to predict major ozone depletions recently seen over Antarctica, we should recognise that current models may not be acceptable even as crude indicators of future trends in atmospheric composition.

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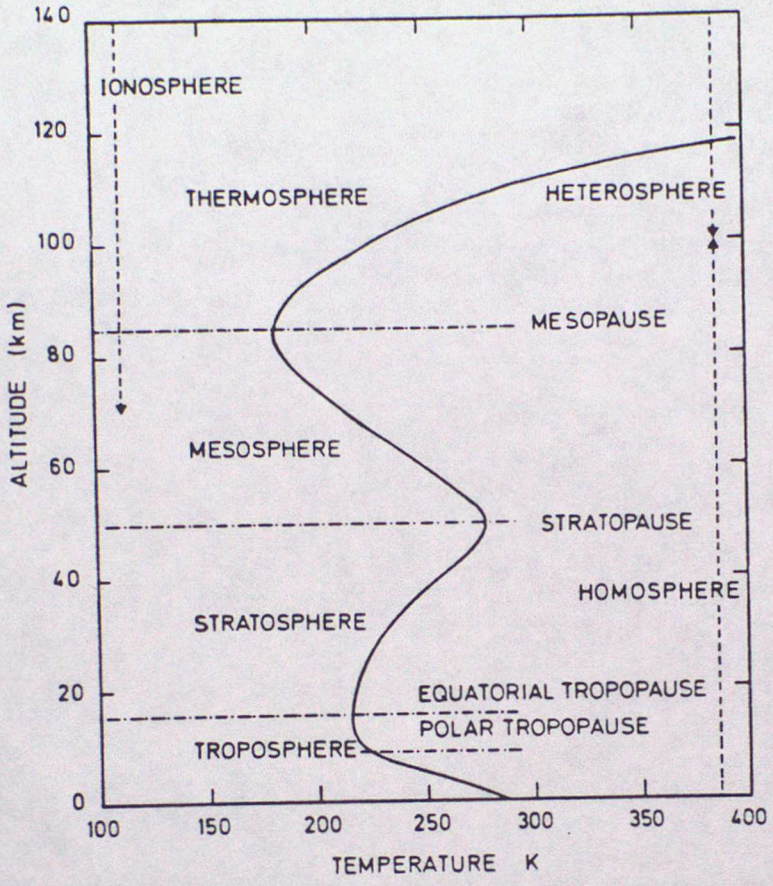


Figure 1 Simplified thermal structure of the atmosphere.

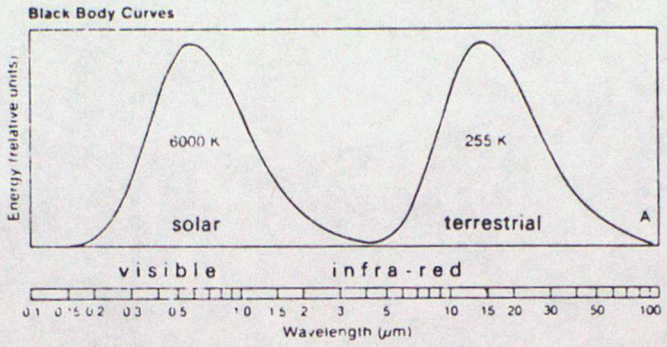


Figure 2a) Wavelength distributions of solar and terrestrial radiation energies. The almost complete separation allows them to be treated independently.

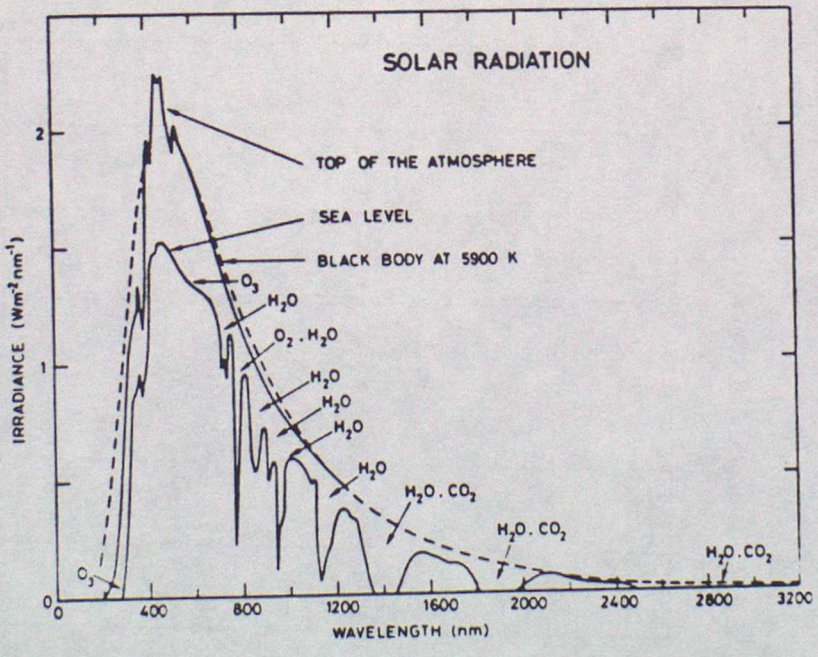


Figure 2b) Spectrum of solar radiation (UV, visible, IR) outside the atmosphere and at sea level.

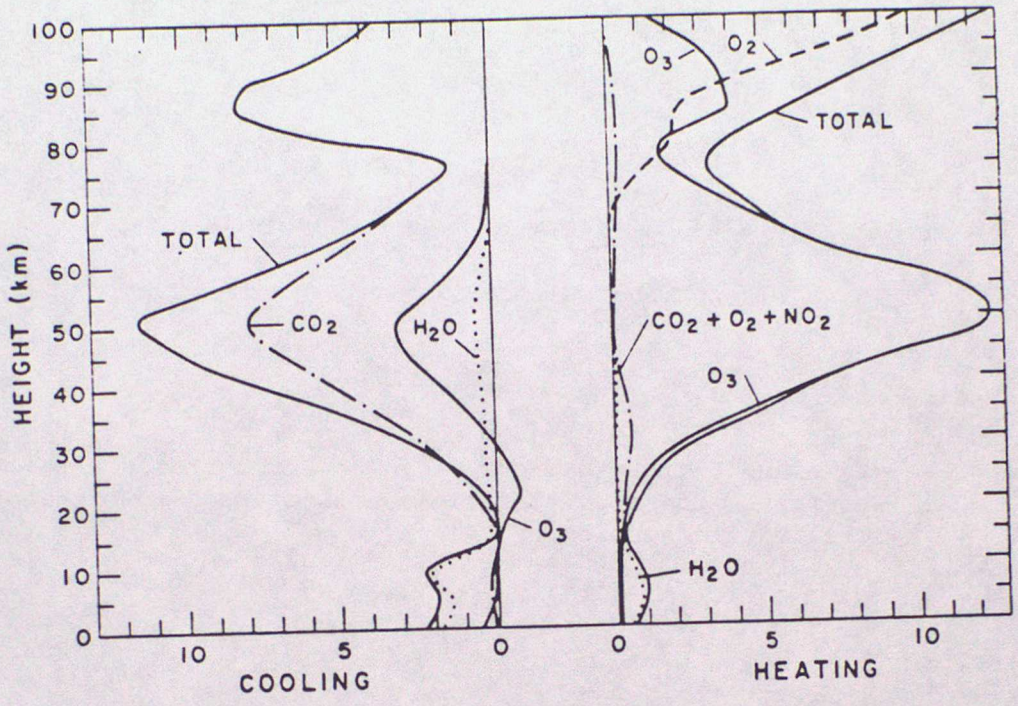


Figure 3 Components of the global average radiative heating and cooling (0-100km) in °K/day.

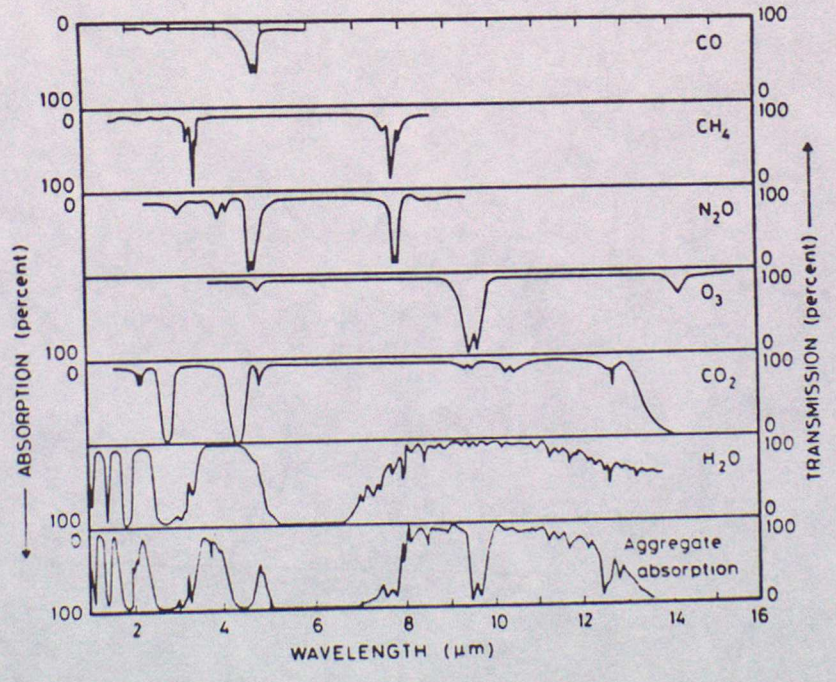


Figure 4 Spectral distributions of the infra-red absorptions of the principal radiatively active gases (from the earth's surface to infinity). The net absorption is shown in the bottom panel.

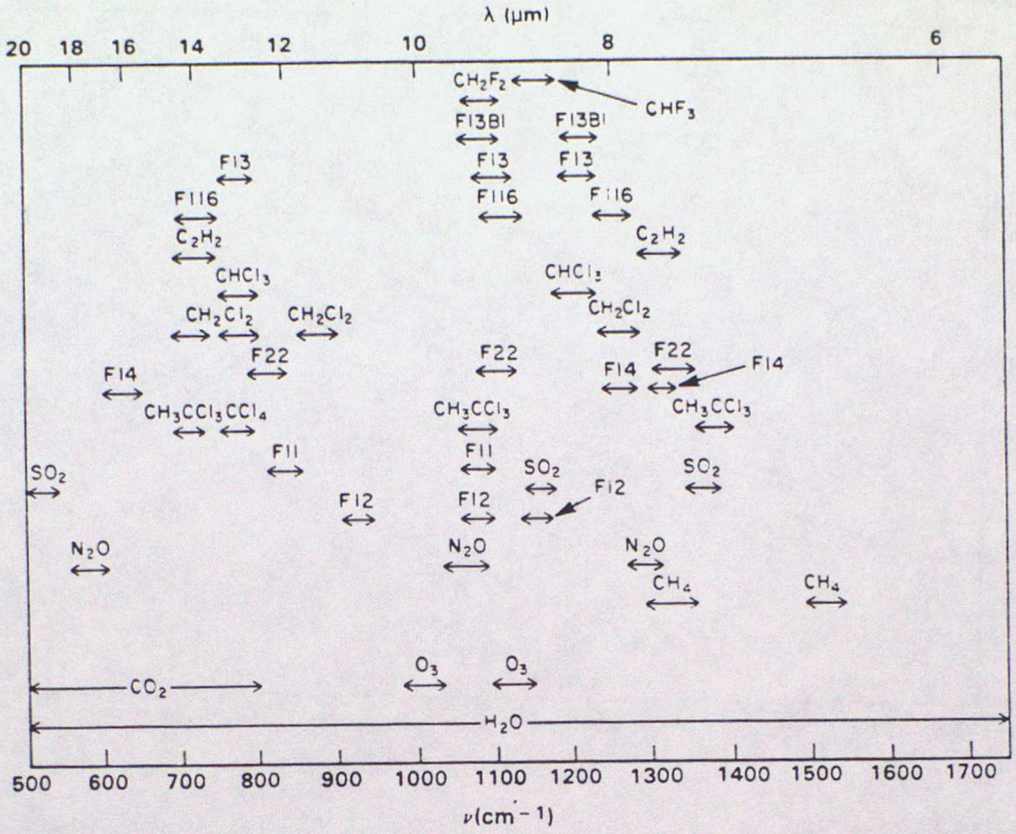


Figure 5 Spectral locations of the absorption features of various trace gases in the region of the atmospheric window (7-13μm).

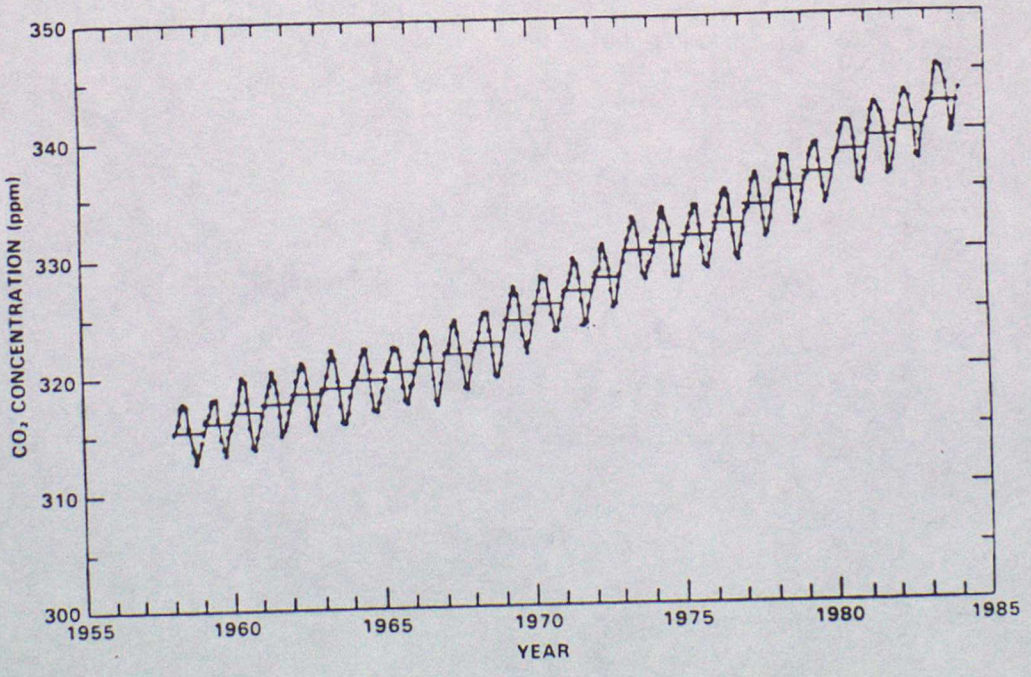


Figure 6 Concentration of atmospheric CO_2 at Mauna Loa Observatory, Hawaii (ppmv). The dots are monthly averages and the horizontal bars annual means.

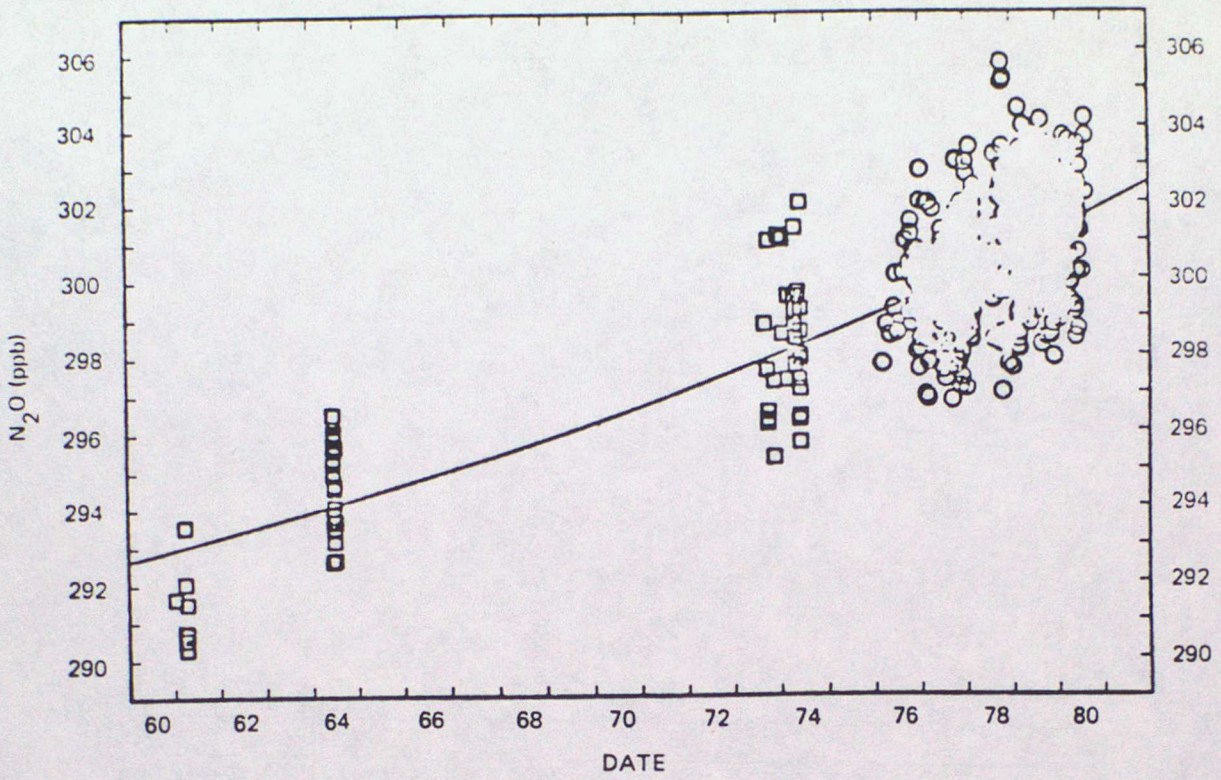


Figure 7 Trend in atmospheric N_2O concentrations (ppbv) since 1960.

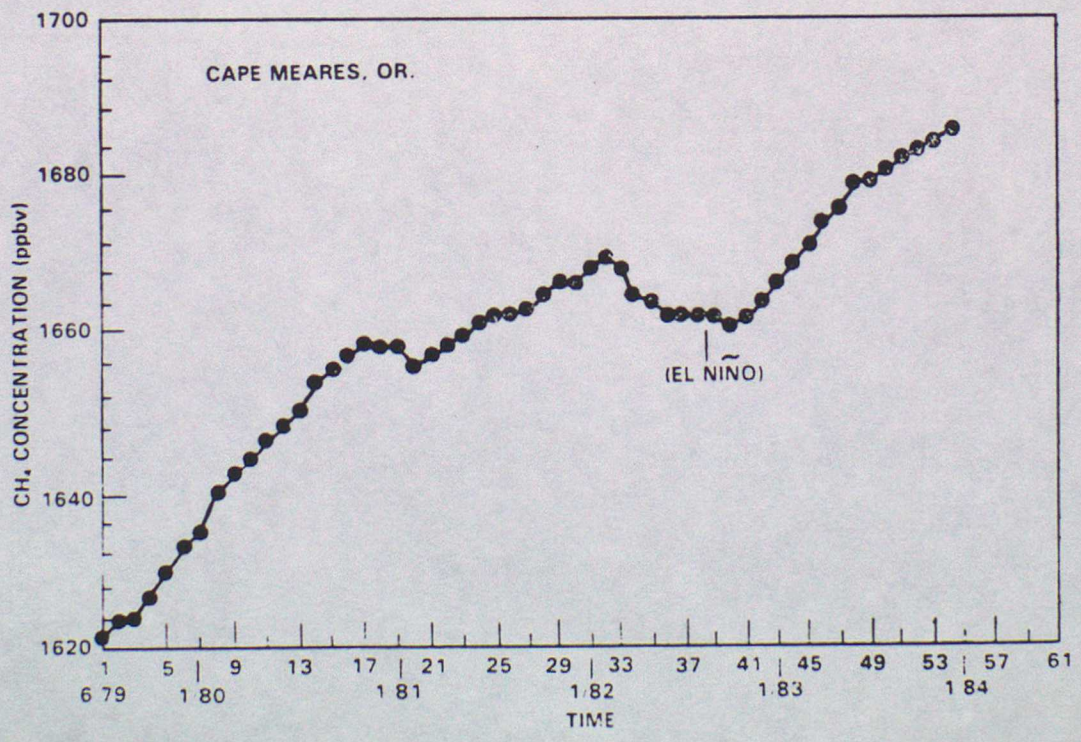


Figure 8 Trend in atmospheric CH_4 concentrations (ppbv) since 1978 as measured at Cape Meares, Oregon. Seasonal fluctuations have been removed by a 12 month running mean. Interannual variations, e.g. possibly associated with the 1982/3 El Nino are apparent.

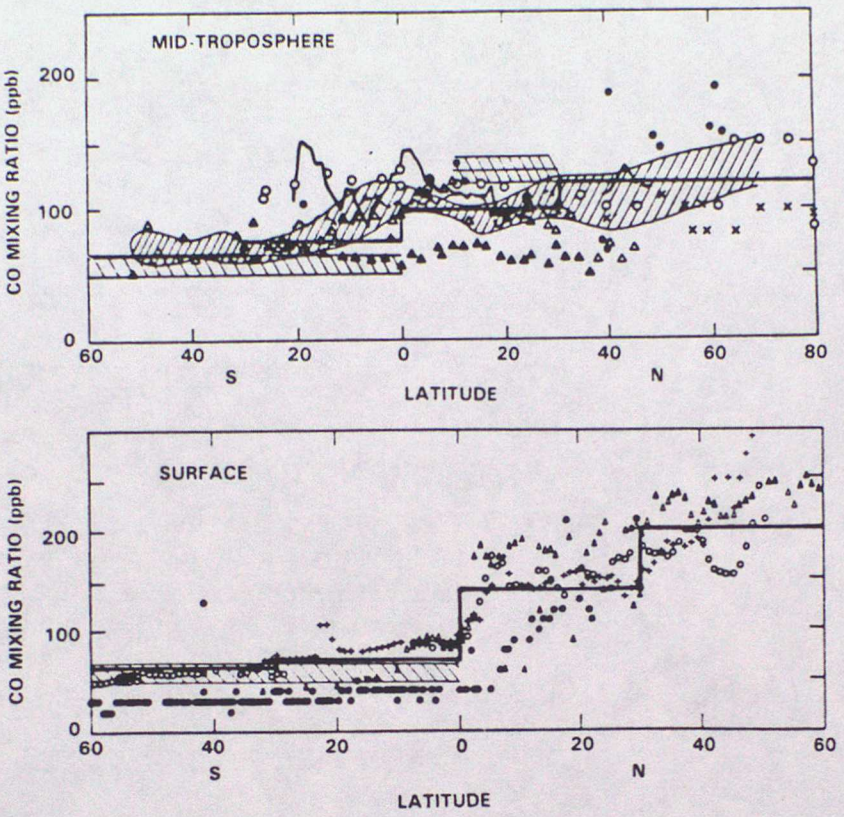


Figure 9 Summary of atmospheric CO concentrations for the mid troposphere and surface for the period 1967-78. The large interhemispheric gradient reflects the predominantly Northern Hemisphere sources.

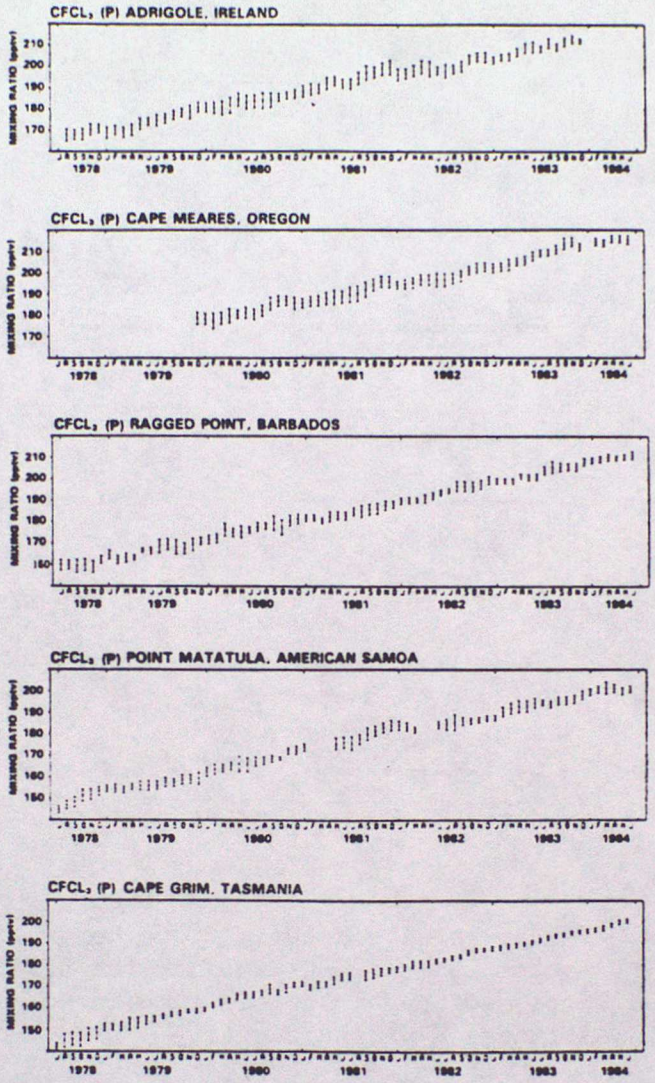


Figure 10a) Surface concentrations (pptv) of CFC-11 measured by the ALE/GAGE network since 1978. Trends since 1978 at the five stations are 4.6, 4.3, 4.8, 5.7 and 5.2 % per year.

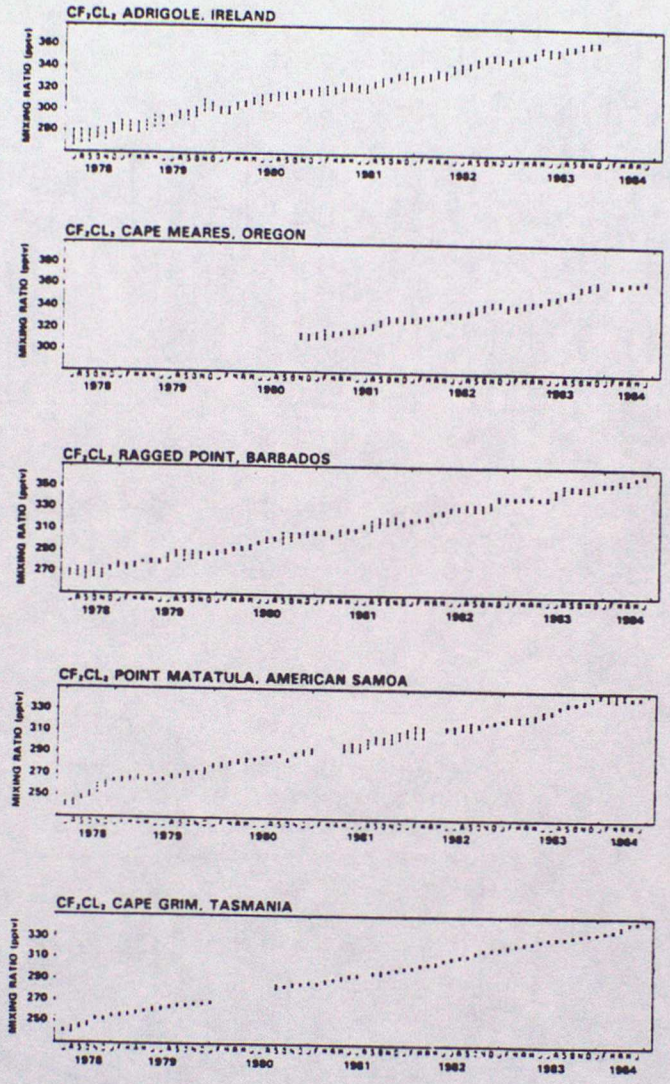


Figure 10b) As Figure 10a) except for CFC-12. Trends are 4.7, 4.6, 5.2, 5.1 and 5.2 % per year.

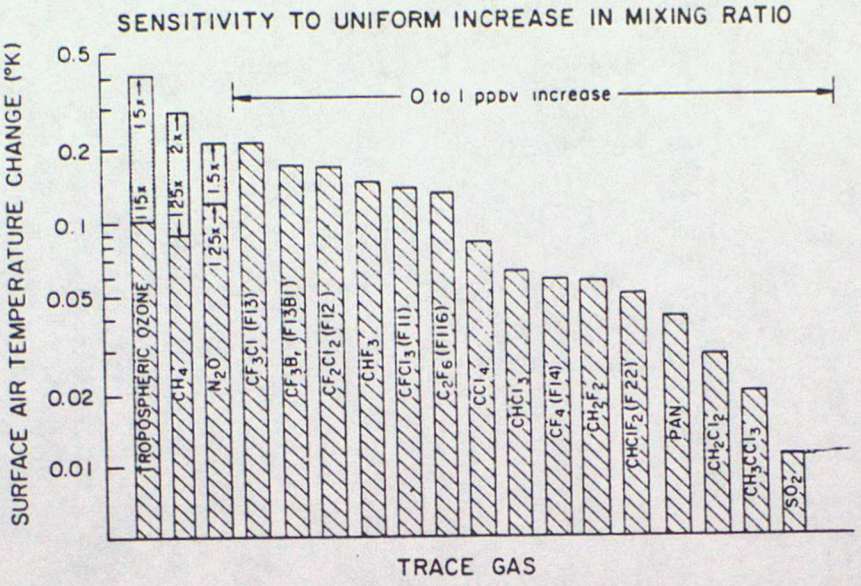


Figure 11 Surface temperature changes predicted by a 1 d RCM model for 0-1 ppbv increase in several trace gas concentrations. The effects of tropospheric O_3, CH_4 and N_2O increases are shown for comparison.

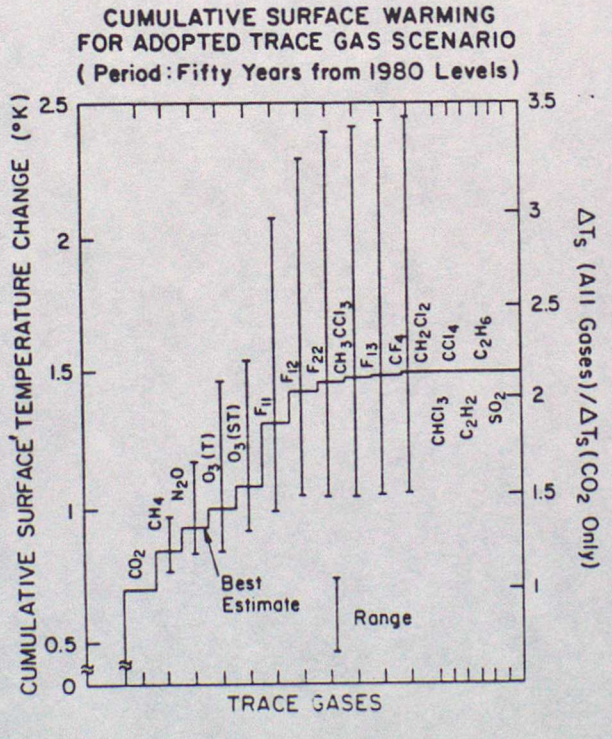


Figure 12 Cumulative equilibrium surface temperature warming predicted by a 1 d RCM model due to specified increases (see Table 1) in CO_2 and other gases, representing the period 1980-2030.

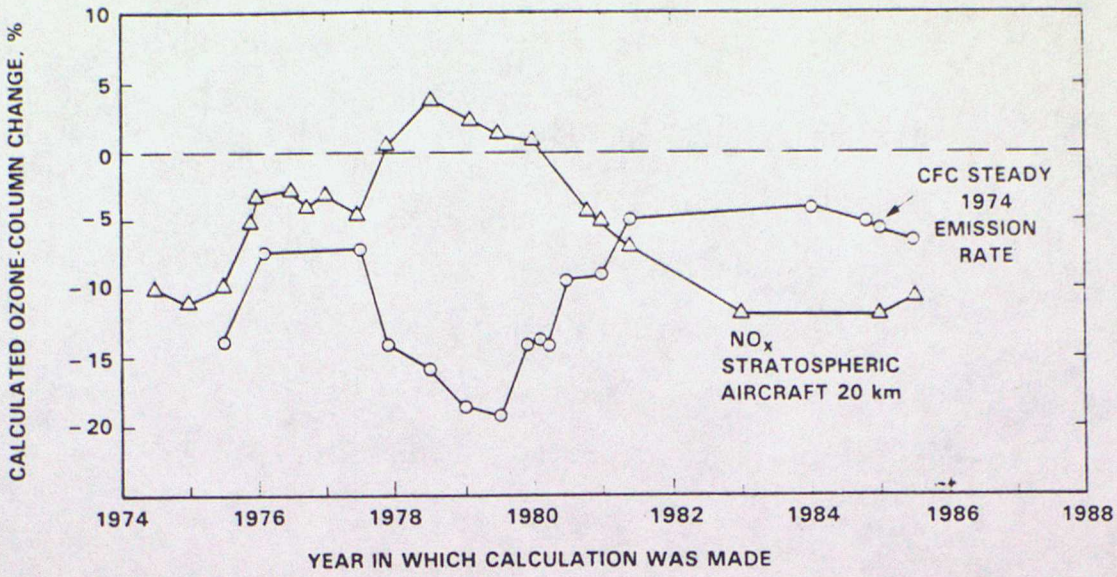


Figure 13 Calculated changes in the ozone column for two standard perturbations 1) NO injection by a large SST fleet at 20km and 2) CFC-11 and 12 held at 1974 emission rates. The changes arise from different photochemical parameters, model transport assumptions and boundary conditions. The major change in 1977 arose from an increased $NO+HO_2$ rate.

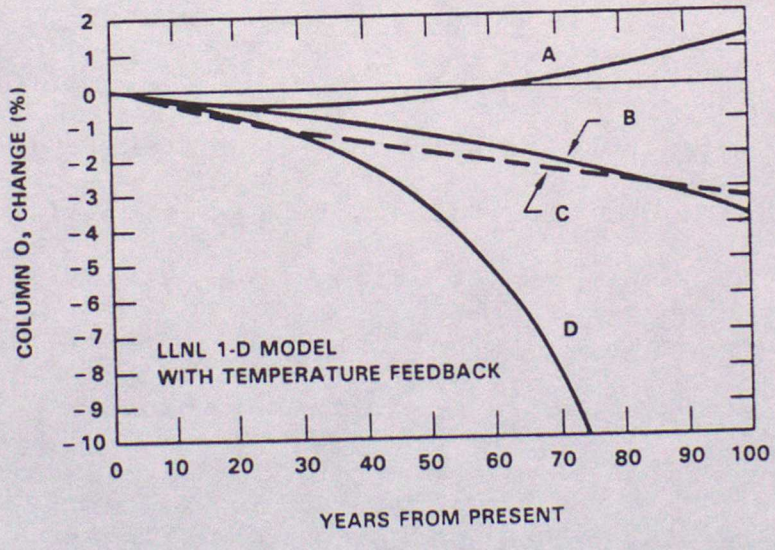


Figure 14 Calculated changes in ozone column for different source gas growths.
A: CFC flux held at 1980 level, CH_4, N_2O and CO_2 increasing at 1, 0.25 and ≈0.4 %per year respectively.
B: As A except no change in CH_4 and N_2O.
C: As A except CFCs increasing at 1.5 % per year.
D: As A except CFCs increasing at 3.0 % per year.

2. The Major Cycles

2.1 Introduction.

The main purpose of this lecture is to discuss the processes which modify and govern the major components of the atmosphere namely N_2 and O_2. However before getting involved with the details it is worth considering one or two basic facts.

2.2 The Geological Cycles.

In some of these lectures we discuss the so called 'geochemical cycles', though we have yet to established that the transfer of material is cyclic.The Earth could just be a ball of hot matter slowly cooling as is radiates away its nuclear energy to space, and gradually running down. Some of the most compelling arguments that this is not the case centre round the time it would take for various processes to run to completion at present rates. The rate of weathering of surface rocks would only take about 70 million years to completely erode the Earths continents and fill the oceans with mud (Turekian,1972), yet weathering processes have been going on for billions of years. As a corollary, the oldest sediments that have been found are only 100 million years old. Another example would be the ocean slaninity.With current sources it would take about 70 million years for the oceans to reach current levels of salinity.Both these processes would suggest that there have been many cycles of the appropriate materials.

Before going any further it is worth while considering some units and terminology which will be useful when discussing many of the chemical transformations which are at the heart of the geo-chemical cycles.

2.3 The gram atom.

It is conventional to express the mass of a particular element in terms of gram atoms this is the actual mass of the element expressed in grams divided by the atomic weight of the element, i.e. the number of moles of atoms (1 mole = 6×10^{23} atoms). The gram atom has the advantage of convaying the approximate mass of a reservoir but also one can compare the relative size of reservoirs in terms appropriate to chemical reactions (stoichiometry), i.e. the gram atom preserves the relative proportions required for complete chemical reactions. e.g. 1 g atom C reacts with 2 g atom O to produce 1 g molecule CO_2.

2.4 Oxidation and Reduction.

As the name implies oxidation is the process of increasing the oxidation state of a substance, reduction (which has a specific chemical meaning) is the process of lowering the oxidation state of a substance. The oxidation state of an atom within a molecule or molecule itself can be deduced from some simple rules.

o The oxidation state of a element is zero, i.e. Na, Cl, H_2, O_2.

o The oxidation state of a neutral molecule is zero.

o The oxidation state of a charged molecule is equivalent to charge of the molecule including sign.

o The oxidation state of a molecule is the arithmetic sum of the oxidation states of the individual elements.

o The oxidation state of oxygen in most molecules is -2.

o The oxidation state of hydrogen in a molecule is +1.

Thus the carbon in carbon dioxide (CO_2) is in oxidation state +4 and is in the same oxidation state as the carbon in the carbonate ion (CO_3^{2-}). The oxidation state of both would be represented as C(IV) and would be described as the fully oxidized state. The oxidation state of the carbon in methane (CH_4) is -4 i.e. C(-IV), and would be described as fully reduced.

2.5 The Equilibrium Earth.

One of the simple ways we can consider the Earths atmospheric system, is to compare the state of the atmosphere relative to an atmosphere in chemical

equilibrium, or we could compare the Earths atmosphere with the atmospheres of Mars and Venus, the planets adjacent to the Earth. Table 1 sets out the relative proportion of each the three most common molecules in the dry atmosphere, of each planet. We see that both Mars and Venus have atmospheres dominated by CO_2, a small amount (relatively) of N_2 and hardly any free oxygen. Neither atmosphere resembles the Earths atmosphere chemically. The Earths atmosphere is mostly N_2 and O_2 with very little CO_2. The most obvious external difference between Earth and its neighbours is that the Earth supports life. The chemical disequilibrium apparent in Earths atmosphere is a direct consequence of that life. To clarify just how out of chemical balance the Earths atmosphere really is consider what would happen if all life on Earth were to be deleted.

Data from (Wayne, 1985)

Planet / Gas	Venus	Earth	Mars
CO_2	0.965	3×10^{-4}	0.953
N_2	0.035	0.781	0.027
O_2	2×10^{-5}	0.209	1.3×10^{-3}

o The oxygen in the atmosphere would initially be depleted by oxidation of the dead reduced organic matter in the oceans and on the land, oxidizing all the carbon to CO_2. This would take about 20 years and would decrease the oxygen content of the atmosphere by 1%. Thus oxygen levels would quickly drop to 20% and CO_2 would rise from 0.03% to 1.03% (Broecker, 1970).As CO_2

is a green house gas this would cause massive perturbations to the climate since the oceans would take much longer ~1000yrs to respond and take up the extra CO_2 into the deep water reservoirs. This effect would be countered to some extent by increases in albedo due to increased cloud cover. Just what the new equilibrium temperature would be, is hard to predict.

o The oxygen decrease would continue, but now more slowly, as oxygen is used up in the weathering of freshly exposed reduced minerals, including organic carbon. It is estimated this would consume all the oxygen in the atmosphere when about 4% of the reduced material had been oxidized.

Consequently the Earth would achieve a 20% CO_2 atmosphere after several million years.

o Oxidation of reduced material would continue at an even slower rate as photolysis of water vapour followed by Jeans escape for hydrogen to space would continue to provide a small source of molecular oxygen.

o Processes in the upper atmosphere which convert N_2 to the more stable nitrate form would continue to operate. However since all the processes which convert nitrate to nitrogen gas are biological there would over the time scale of several million years be an accumulation

of nitrate ions in the oceans.

The final state of the Earths atmosphere would be quite different from what we know today. Clearly the life on Earth is not just a passive passenger on the surface, even though that life only constitutes a tiny fraction of the mass and volume of the planet.

2.6 The Oxygen cycle.

Many basic biological and chemical processes rely on the availability of oxygen to release chemical potential energy. Consequently oxygen is the most important gas with which we will deal. There are three main oxygen reservoirs which one must consider. The magnitude of these reservoirs and the size of the fluxes between these reservoirs are shown in Fig 1.

The Atmosphere.

The main oxygen containing species in the atmosphere is O_2. In the stratosphere a small fraction of this is photolysed, ultimately leading to the formation of ozone and the ozone layer. The current atmospheric oxygen content is 0.79×10^{20} g atom O.

The Hydrosphere.

The oceans are the biggest reservoirs of oxygen, very little oxygen is dissolved in the water

but the water itself constitutes a vast reservoir of 761×10^{20} g atom O.

The Lithosphere.

The lithosphere is made up of the Earths crust and the top of the mantle,this is the region where most of the compounds which take part in the geochemical cycles reside, very little actually reachs the underlying mantle.

The lithosphere is the next biggest reservoir with water making up 177×10^{20} g atom O. Oxidized sediments are by comparison a small but significant reservoir with 6.0×10^{20} g atom O in ferrous oxide (FeO) and 8.5×10^{20} g atom O in sulphates (SO_4^{2-}). Ferrous oxide is actually a net sink for oxygen because on exposure to air it reacts with oxygen to form ferric oxide (Fe_2O_3), which is the prefered state in an oxidizing atmosphere.

The Pedosphere.

The soil layer, usually taken to denote the terrestial surface layer where the various life activities go on and the organic matter resides. The pedosphere does not constitute a reservoir for oxygen but exchanges with this region are an important factor in the oxygen cycle. The main fluxes of the oxygen cycle are shown schematically in Fig 2.

Relative to the reduced sediments such as FeO

and organic carbon the atmospheric reservoir would appear to be quite small. There is more than enough reduced material to completely consume the oxygen atmosphere. Since these reduced materials have been recycled many times in the Earths history we can conclude that most of these reduced materials have been isolated from the Earths atmosphere for many millions of years.

2.7 Photosynthesis

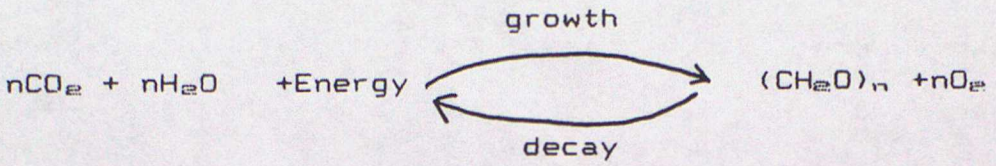
The most rapid cycle which we need to concern ourselves with is the photosynthesis/respiration cycle. This is the mechanism whereby green plant material converts carbon dioxide and water vapour into sugars and oxygen. For our purposes we can represent this process by the chemical equation:

$$nCO_2 + nH_2O + \text{Energy} \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftharpoons}} (CH_2O)_n + nO_2$$

Photosynthesis requires sunlight and so only operates during daylight hours. Thus we have nett oxygen production during daylight and nett oxygen consumption during darkness. This cycle is thought to be in balances neither adding to nor removing from the atmosphere any significant amount of oxygen.

These sugars are produced by plants to provide energy in a suitable form to facilitate plant growth.

The growth cycle operate on a longer time scales and can still be crudely represented by the following equation.



The rate of production of sugars will ultimately control the growth of the more permanent organic material. Organic material will be cycled over a variety of much longer time scales, e.g. the life cycle of a plant, the growing season, a few growing seasons, and the time it takes for woody material to decay, but all the oxygen released by the formation of organic material will eventually recombine with the terrestial organic material to form water and carbon dioxide, and so again longterm there is neither a nett loss or gain of reduced carbon .

Consider this in terms of the oxidation states of carbon. In CO_2 carbon has an oxidation state of +4 and in the sugars $(CH_2O)_n$ it has an oxidation state of zero. At the same time the oxygen atoms in CO_2 each change there oxidation state from -2 to zero, forming molecular oxygen, i.e every time there is a nett reduction in the oxidation state of carbon of 4,there will be a compensating rise in the oxidation states of some other material,if this is oxygen then it will result in the formation of molecular oxygen.Since we think that the equilibrium chemical state of the

atmosphere is for there to be no free oxygen we must account for each free oxygen molecule by the equivalent of at least an equal number of carbons in a fully reduced state.The reverse process of increasing the oxidation state of carbon takes place in respiration or oxidative decay.

We should see that the terrestrial biosphere is a dynamic reservoir. As the biosphere grows more of the carbon in atmospheric CO_2 is reduced and free oxygen is released, at the end of each growing season this process will be partially reversed. However, as some forms of reduced carbon take much longer to be oxidized back to carbon dioxide, this return may be over many growth cycles (it is estimated that it takes 20 yrs to oxidize woody material totally). If all the reduced carbon in the biosphere were oxidized it would only decrease the abundance of atmospheric oxygen by 1% percent. While this is a significant reduction, it is quite inadequate to explain present atmospheric oxygen levels, arising as a result of terrestial photosynthesis and the production of terrestial reduced carbon. How did all this free oxygen get into the atmosphere then since there is not nearly enough reduced carbon in the biosphere to account for the present O_2 levels? (Broecker,1970)

2.8 The Oceans.

The marine biosphere also goes through the same processes as the terrestial biosphere but the

oceanic biomass is even smaller than the terrestial biomass and so can not (by virtue of its bulk) account for the extra oxygen.

There is however,one process which takes place in the oceans but which does not have a direct parallel with the terrestial biosphere, and this process is a nett source of O_2. In the atmosphere oxygen is always in excess which means that material which is available for oxidiation is always oxidized, consequently no long term reduced carbon reservoirs can build up. The same does not apply to the oceans. All the photosynthetic activity in the oceans is concentrated in the upper levels, the concentration of oxygen in the upper levels is controlled by the partial pressure of oxygen (pO_2) of the overlying atmosphere and by the balance between respiration/photosynthesis and growth/decay in the oceans.

It is to the growth/decay cycle in the oceans which we should look at more closely to find the source of atmospheric O_2. When a marine animal grows it ties up some of the carbon in a reduced form and so releases free oxygen. When the organism dies this reduced carbon will begin to oxidize. The carcass however will also begin to settle to the sea floor. As it does so the oxygen concentration of the water will decrease as it moves further away from the oxygen source regions (see Fig 3). The oxygen content of the water will be further depleted by the oxidation of the reduced organic carbon.Ultimately the oxidation will stop as truly anaerobic conditions are encountered. Some of this

reduced organic carbon will settle in sediments and form the reduced carbon content of mineral and fossil fuel deposits. It is this fossilized reservoir which ties up sufficient reduced carbon to allow the high levels of O_2 which we at present experience. (Van Valen,1971)

Over geological time scales, through the process of lithofication these sediments form rocks, and are ulitmately returned to the Earth surface where chemical weathering oxidizes the carbon back to CO_2, consumes O_2, and completes the cycle.

2.9 The Evolution of the Oxygen Atmosphere.

We have considered the present day oxygen cycle and briefly how that cycle would be modified if life we removed, now we will consider how the atmosphere evolved to its present composition. In the earliest atmosphere there was no free oxygen. Prior to that time the atmosphere was slightly reducing being mostly CO_2 and N_2 with some ammonia , methane and hydrogen, all from volcanic sources. The anaerobic lifeforms which were present at that time were restricted to the oceans. Indeed they could only occupy a small fraction of the available ocean volume because the harsh uv-radiation from the sun would make the upper layers of the ocean uninhabitable (no free oxygen, no ozone layer). These early life forms did not use photosynthesis as a source of energy but would extract a little energy from the trace chemicals which

were produced by random chemical processes, or emitted from the earths interior.

About 600-800Myrs ago stromatolites (a form of algea colony) evolved a way of using water (which was readily available) as a substitute,when they photosynthesised, for the hydrogen which was less freely available. This lead to the release of molecular oxygen as a by-product [Initially bacterial photosynthesis reqired only a reducing gas like H_2 and did not produce any oxygen. However, the supply of hydrogen had always been limiting , so these life forms could not develop very vigourously (Walker,1977,p249)]. The oxygen emitted by these colonies would began to accumulate in the atmosphere until it reached about 1% of present day levels. It is estimated that, when these oxygen levels were reached,oxygen, and ozone formed in the atmosphere, would provide sufficient sheilding to make the upper layers of the ocean inhabitable. This would be followed by an explosion of new growth in these areas but only by species which were oxygen tolerant. This extra growth would result in major increases in the oxygen content as organic carbon would fall to the ocean floor away from the oxygen rich surface in ever increasing quantities. The oxygen levels would continue to rise until the increases were sufficient to oxygenate the layers of the ocean that had hitherto been anaerobic, and so reoxidize some of the dead organic matter.

It should be clear that the oxygen in the atmosphere depends crucially on the activities of the

biosphere, in particular the marine biosphere, and that any new equilibrium which would be established without life would be quite different from the present atmospheric composition. What might not be so clear is the role of reduced carbon in this controlling process. This will be taken up again in lecture 3 on the carbon cycle .

2.10 The Nitrogen Cycle.

Nitrogen is one of the elements along with C,O,S,P which is fundamental to life. Most biochemical activity requires nitrogen containing molecules. The atmosphere is 79% nitrogen, yet it is nitrogen in a form which is unusable by almost all biota. Nitrogen is also a molecule which is not in its thermodynamically most stable form. In the present atmosphere the hydrogen ion concentration (pH) and the oxidation state of the Earth (pE) are such that nitrogen should exist as NO_3^- in solution (Delwiche,1970).

Estimates of the oxygen production of various geographical areas and ecosystems have been carried out exhaustivly and so global estimates of O_2 production can be considered quite reliable. This is not the case for the various processes which govern the release and up take of nitrogen species. These are by comparison poorly understood. Nitrogen can exist in a several oxidation states, making its chemistry complex. We will however restrict our discussion to the transformations which are considered most important [since most of these processes are mediated by biota even the chemistry is poorly understood] .

2.11 The Nitrogen reservoirs.

Atmosphere: Almost all atmospheric nitrogen is in the form N_2 i.e. 2.8×10^{21} g atom N all other compounds of

nitrogen are only present in trace quantities.

Oceans: The inorganic nitrogen content of the oceans in the form of the nitrate ion (NO_3^-) is very small with only 7×10^{15} g atom N.

Lithosphere: There is a large quantity of nitrogen incorporated in reduced organic sediments. However there is still considerable confusion as to the absolute size of this reservoir. Highest estimates (10^{20} g atom N) would suggest that it is still only a small fraction of the atmospheric reservoir.

The smallness of the oceanic reservoir is paradoxical since the N_2 in the atmosphere is not thermodynamically stable w.r.t the solvated nitrate ion in the oceans. The nitrogen oxidation reaction does not go because of the very large activation energy of the reaction, however, there is sufficient photochemical oxidation to have oxidized the atmospheric N_2 over geological time scales. Hardly any nitrate exists in the ocean, where it is a valuable nutriant and always in short supply. If nitrate were allowed to accumulate in the oceans some other nutrient would become limiting and so no extra growth could be sustained with just an excess of nitrate. Fig 4 shows a schematic representation of the nitrogen cycle.

Since man has started to influence his immediate environment , he has perturbed many of the major biogeochemical cycles. To date these

perturbations have been relatively small, however in the case of nitrogen, Man is now the biggest producer of 'fixed' nitrogen, i.e.nitrogen which is converted from inert N_2 into active forms such as Ammonia (NH_3) and nitrate (NO_3^-).He has 'achieved' this by industrial fixing of nitrogen in the Haber process and by the cultivation of legumous crops (plants which are in a symbiotic relationship with nitrogen fixing microbes) e.g. peas. There are also contributions from photochemical production and lightning but these are small by comparison. Most of this fixed nitrogen is either denitrified back to N_2 by specialised microbes in the soil or is transfered to the oceans as the stable nitrate ion.

Once in the oceans this nitrate is incorporated into organic tissue and some of it will eventually be buried in the ocean sediments. However estimates of how much fixed nitrogen is removed in this way suggests that there should be another oceanic sink of nitrate, converting it back to N_2. This sink is denitrifying bacteria which use NO_3 for respiration type processes if there is a shortage of O_2. The size of this flux is not well known, it is usually estimated by assuming it is just large enough to balance the nitrogen cycle, however it is important that we know whether the oceans are able to denitrify all the extra nitrogen which we have been adding for many years since it is very likely that this could upset the ecological balance in the oceans.

Most of this conversion is back to N_2

directly, however some species only part oxidize N_2 and produce nitrous oxide N_2O. Fig 5 shows the profiles of N_2O and O_2 observed in the Atlantic (Hahn,1974). N_2O has no significant chemical or physical sinks in the troposphere so it can reach the stratosphere, there most is photolysed to give N_2 and O but some will react with excited oxygen atoms and form nitric oxide NO which has a significant role in stratospheric chemistry. Just what processes govern the production of N_2 as apposed to N_2O are not clear, but it is interesting interaction between two quite distinct parts of the Earth system It is also worth noting that mans activities have had a major impact on the N_2O budget and are now thought to be the major sources. Estimates suggest that the anthropogenic sources (power stations, forest fires, etc) are, in total, about twice the size of the oceanic source.

From this lecture you should now have an idea about the effects which operate to regulate the gross composition of the atmosphere. You should be in no doubt as to the importance of some organisms in relation the atmospheric composition. It would appear that these organisms exercise a controlling influence on very long time scales. However, we should be aware that an apparent controlling influence may only be a manifestation of the stability of the system at present and has no more profound meaning than some other non-biological influence.

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Fig 1

Oxygen Cycle

Reservoirs 10^{12} g atom O

Fluxes 10^{12} g atom O per yr

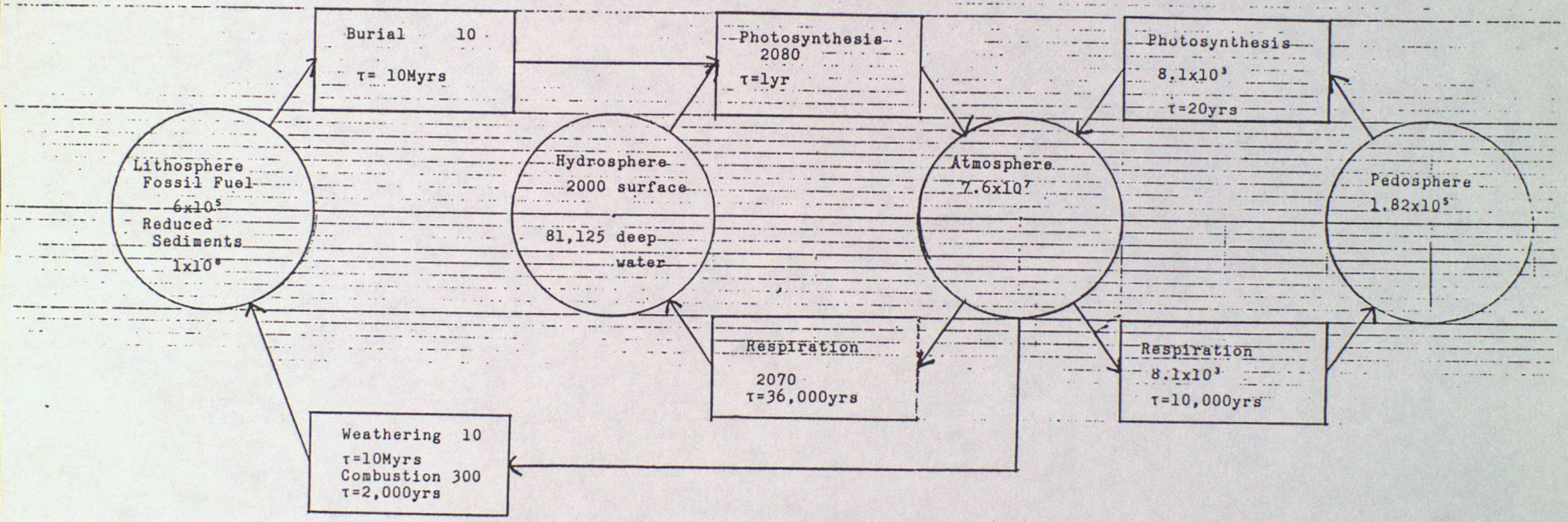
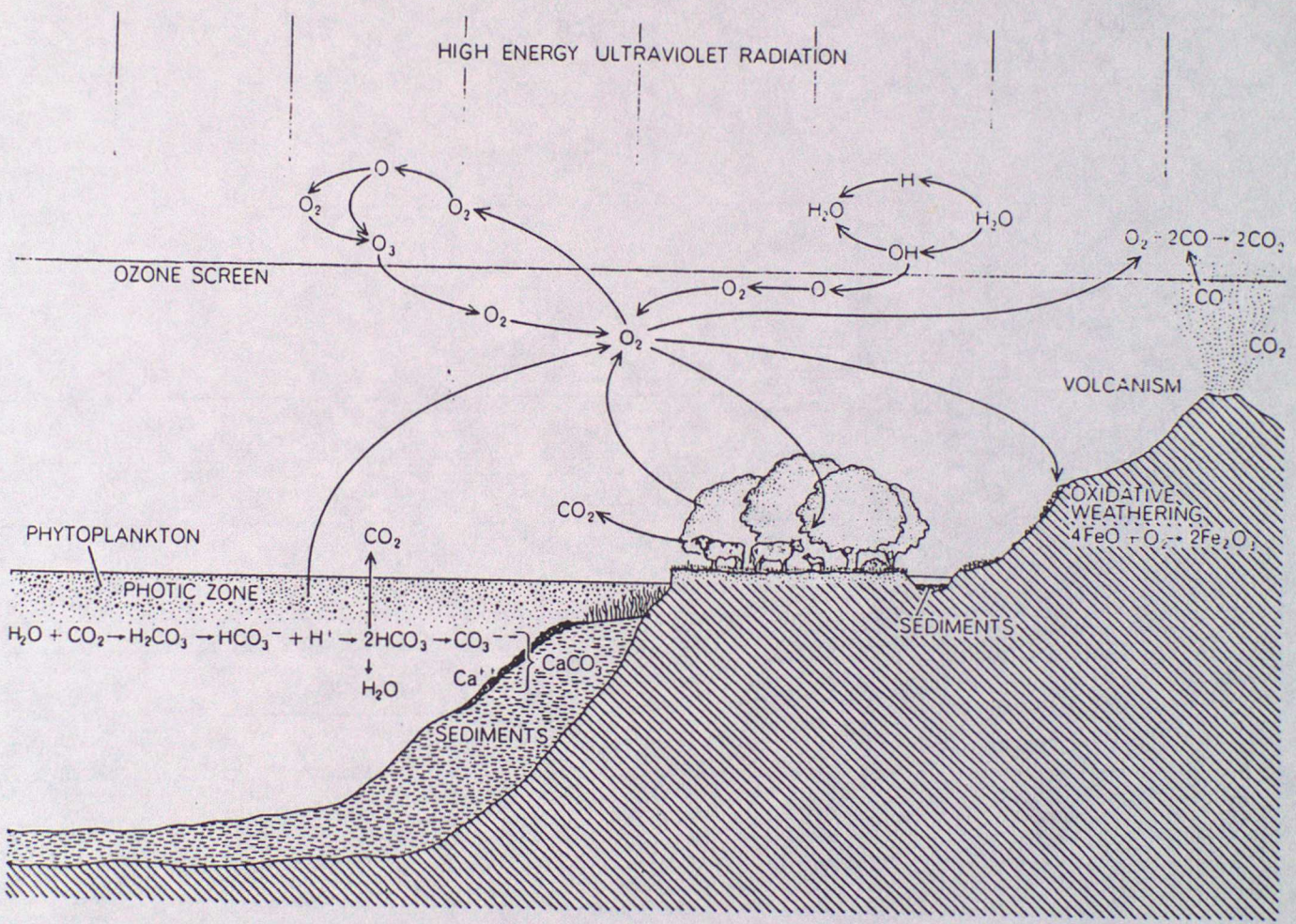
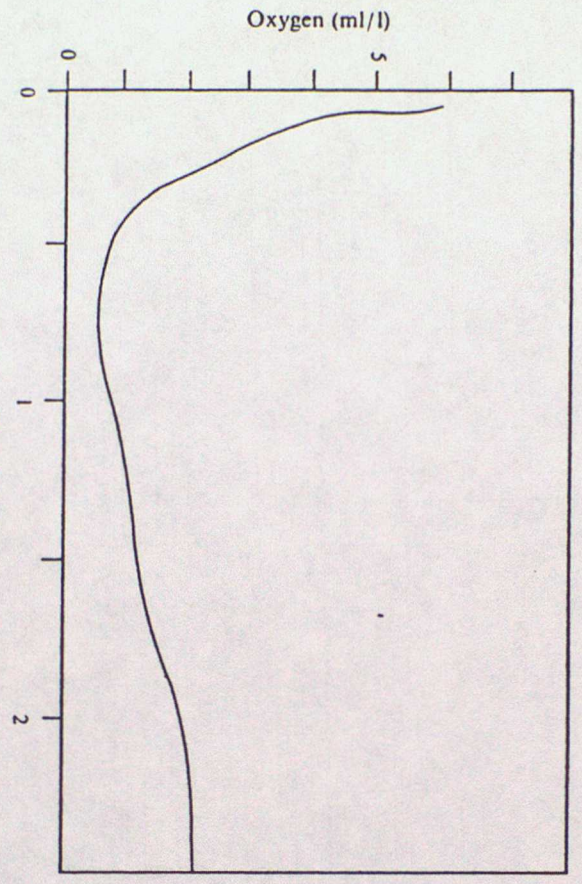


Fig 2



OXYGEN CYCLE is complicated because oxygen appears in so many chemical forms and combinations, primarily as molecular oxygen (O_2), in water and in organic and inorganic compounds. Some global pathways of oxygen are shown here in simplified form.

Fig3



Representative profile of dissolved oxygen as a function of depth in the Pacific Ocean. (After Riley and Chester, 1971.)

Fig 5

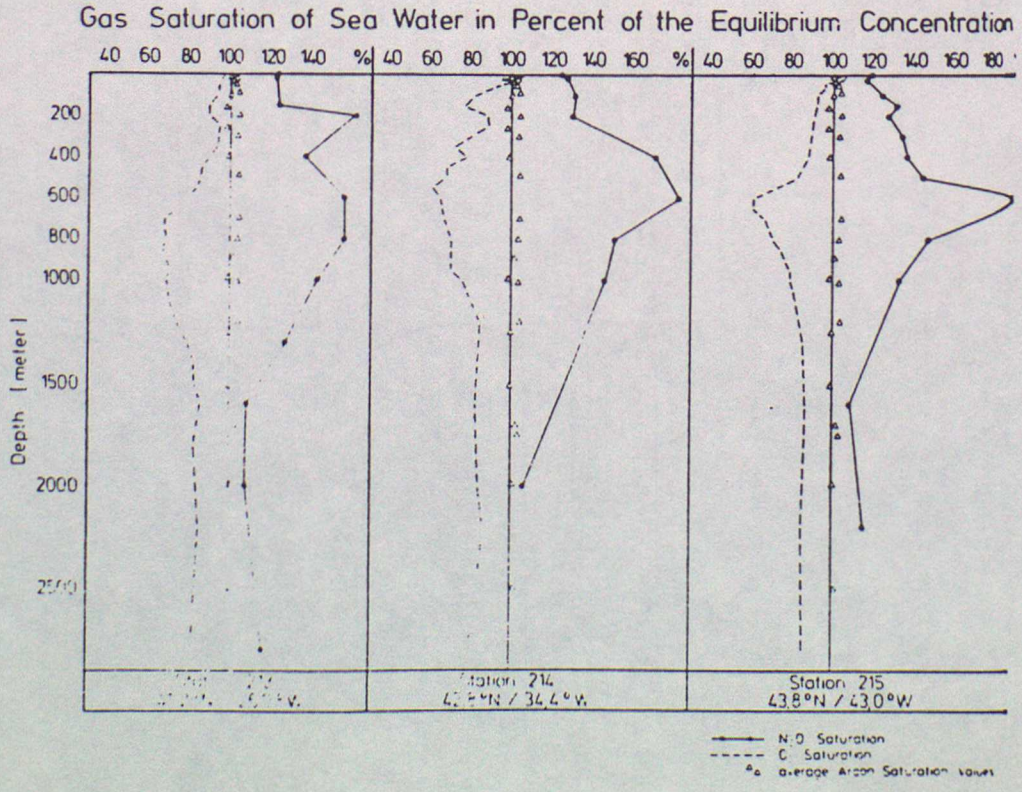
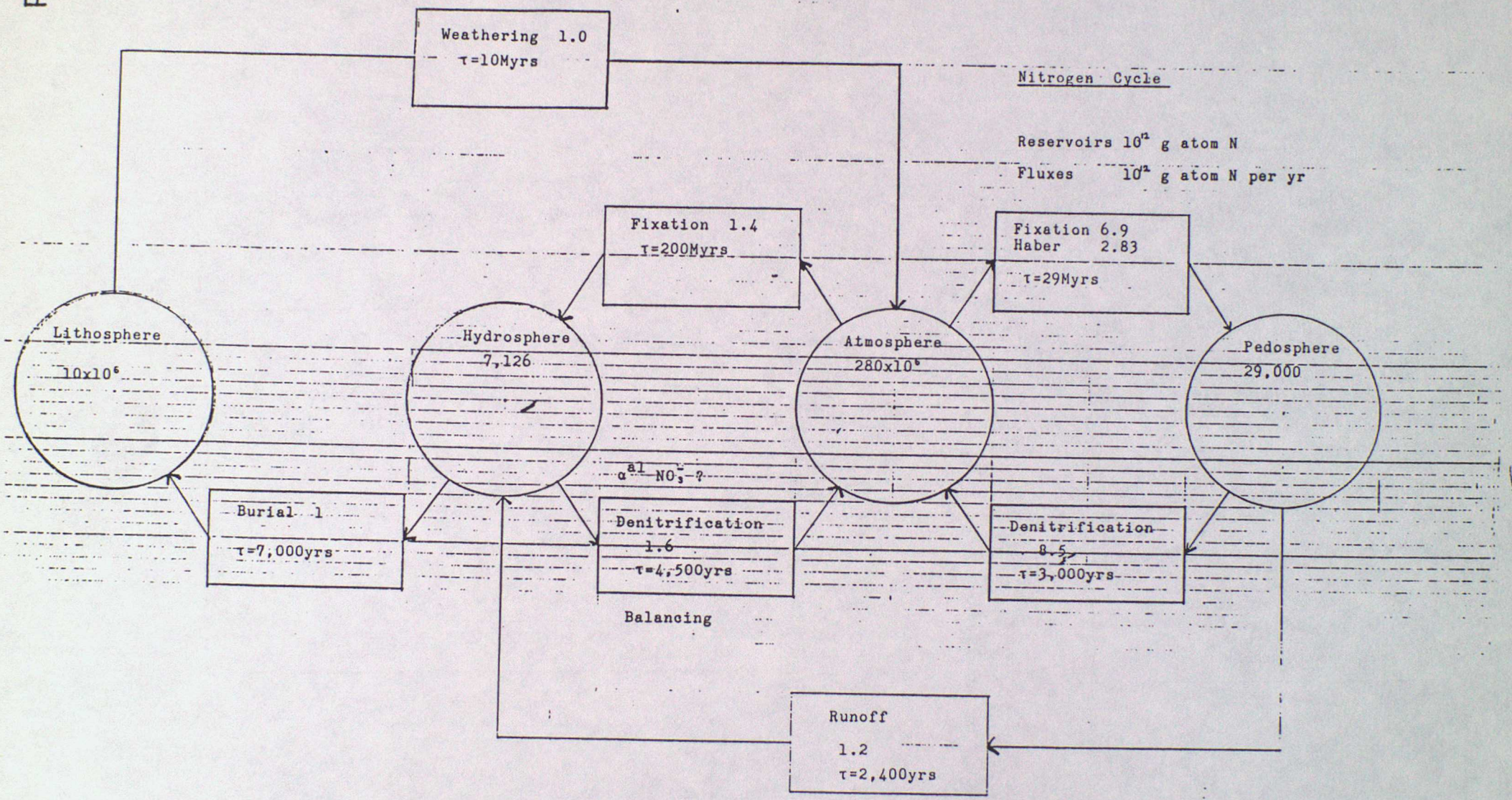


Fig 7


Weathering 1.0
τ=10Myrs
Nitrogen Cycle
Reservoirs 10^{12} g atom N
Fluxes 10^{12} g atom N per yr
Fixation 1.4
τ=200Myrs
Fixation 6.9
Haber 2.83
τ=29Myrs
Lithosphere
10x10⁶
Hydrosphere
7,126
Atmosphere
280x10⁶
Pedosphere
29,000
α^{al} NO_3^- ?
Burial 1
τ=7,000yrs
Denitrification
1.6
τ=4,500yrs
Denitrification
8.5
τ=3,000yrs
Balancing
Runoff
1.2
τ=2,400yrs

3. The Carbon Cycle.

3.1 Introduction.

There are a number of reasons why we should consider the Carbon Cycle as important and worth investigation:

- The radiative properties of CO_2 and the resultant atmospheric effects;temperature and temperature gradient changes, precipitation etc.

- Direct changes in crop productivity due to increased CO_2 levels.

- The effect of higher CO_2 levels on marine biota.

- The feedbacks that any of these direct effects may have on the overall biosphere.

It is impossible to compartmentalize any one aspect of the geochemical carbon cycle.The different aspects are inextricably linked and so complex models must be employed. We have already seen when discussing the oxygen and nitrogen cycles that there are close links between all the cycles - we have already had to consider carbon when discussing the oxygen cycle. In reality when doing the 'book-keeping' for the nitrogen cycle one often relies on the carbon cycle data which is normalised to take account of the approximately

fixed ratios which exist between all the major elements in living matter.

3.2 The Reservoirs.

As a first stage in considering the carbon cycle it is instructive to list and compare the main carbon reservoirs. Throughout this lecture I will use data from a recent report so that at least the numbers are reasonably up to date,consistant and comparable, (Bolin,1986,chpt3). Fig 1 represents the major reservoirs and fluxes associated with the carbon cycle.

Table 1

Reservoir	g atom C $\times 10^{18}$
o Atmosphere:	60,000
o Land :	181,000
o Sea :	3,160,000
o Fossil Fuel:	833,000

The atmosphere is the least structured of the carbon reservoirs. Virtually all the carbon is CO_2, whose radiative properties we should all be well aware (some of the minor carbon species will be discussed in lecture 6 on tropospheric photochemistry).

The land includes all the terrestial biota as well as the dead and decomposing remains, and the carbon contained in the soil. The terrestial biota produce easily decernable signals in the carbon dioxide mixing ratios on a number of time scales (see Fig2,3&4)

which can be related to the photosynthesis and growth cycles in the biosphere.

The sea contains considerable reserves of inorganic carbon as well as contributions from marine biota.

Finally we have the fossil fuel reserves which we are busily converting to CO_2 and releasing to the atmosphere. Estimates suggest that if we continue to consume fossil fuels at the present rates (Fig 6) then reserves may be exhausted in approximately 1000yrs. However if, as is at present the case, we maintain a constant rate of increase in consumption, i.e. exponential growth, then the fuel reserves could be exhausted in approximately 100yrs. Realistically, we might expect that the actual fuel consumption will fall somewhere between these to limits.

Consideration of the size of these reserves very rapidly leads one to the conclusion that if a large fraction of the fossil fuel reserves are converted to CO_2 and this extra CO_2 were to remain in the atmosphere then there would be increases in the CO_2 mixing ratio far in excess of what we have yet experienced.

However things are never as straight forward as that. Release of CO_2 due to man's acitivities has been going on for some time. Both fossil fuel consumption and land use changes have released a great deal of CO_2, which has in turn resulted in a marked increase in atmospheric CO_2. As can be seen from Fig 5, pre-industrial values of CO_2 are believed to have been

about 275 ppmv and by the early 1980's are known to have risen to nearer 343 ppmv, giving a rise of 68 ppmv. Best estimates of how much carbon has been released over the same period are that fossil fuel consumption has released $(15\ 1)\times10^{15}$ g atom C and land use changes have released $(12.5\ 4)\times10^{15}$ g atom C. If all this carbon had remained in the atmosphere we would be experiencing CO_2 levels nearer 440 ppm instead only about 40% of the CO_2 released has remained in the atmosphere. Clearly then there is a nett transfer of CO_2 to the other reservoirs, of these the ocean is the only reservoir which can accommodate that much extra CO_2. So while the oceans are taking up the bulk of this extra CO_2 they are clearly not simply a passive sponge soaking up extra CO_2 as fast as it is released.

3.3 The Oceans.

The marine reservoir is made up of a surface layer which contains about the same amount of carbon as the atmosphere and a vast deep sea carbon reservoir. The bulk of the carbon is dissolved inorganic, however, there are sizable reserves of dissolved organic carbon which exists in a more reduced forms than the inorganic carbon. The existance of organic carbon implies a lack of oxygen in these regions since oxygen in general oxidize the carbon to the inorganic forms (Bolin,1970).

The near surface layer which has much less organic carbon is also where all the marine biota exist. While the biota only tie up a small amount of

carbon at any given moment they are responsible for fluxes of carbon which implies an several exchanges annually of the marine biomass. The biggest fluxes to the marine surface layer arise from its contact with the CO_2 containing atmosphere. The initial uptake of CO_2 by the oceans is governed by the solubility of CO_2 in water, since this is greater in cold water we find that there is a net transfer of CO_2 to the oceans in high latitudes with a balanced return flux from low latitudes. The next largest transfers that we see are from the surface layer to the deep ocean. Much of the transport below the ocean surface is along isopycnic surfaces which play a similar role to the isentropic surfaces of the atmosphere, however the density which defines these surfaces now depends on both temperature and salinity, in the Atlantic these surfaces slope down from the poles to the equator so that there are isopycnic surfaces which are near the surface in high latitudes and which reach middle and deep water at lower latitudes. In the Pacific there is no northerly branch (see Fig 6). It is transfer along these surfaces which accounts for the large downward flux of CO_2, the returning CO_2 is mainly in regions of upwelling. Transfer to the deep ocean will in the fulness of time remove almost all of the fossil fuel CO_2 which we are emitting but it will take a considerably longer than the time scale on which climate change may set in. The transfer from the deep ocean to the surface is very slow. If we measure the age of the water by how long it has been away from the

surface then the oldest Atlantic water is ~1000yrs old, while the oldest Pacific water is ~2000yrs old.

3.4 Aqueous Phase Chemistry of CO_2.

Now we will go back and look at how CO_2 is dissolved in water in more detail. When CO_2 dissolves in water it aquires a water molecule and forms hydrogen bicarbonate

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (1)$$

The concentration of H_2CO_3 is related to the partial pressure of CO_2 above by the relationship:

$$[H_2CO_3] = K_1.pCO_2$$

where $[H_2CO_3]$ represents the concentration of H_2CO_3 and pCO_2 represents the partial pressure of CO_2. K_1 as mentioned earlier depends on temperature, CO_2 being more soluable in cold water than in warm water. At 298K K_1 is equal to 3.4×10^{-2} per atm. Once in solution the hydrogen bicarbonate can dissociate by the following reactions.

$$H_2CO_3 \longrightarrow HCO_3^- + H^+ \qquad (2)$$

with equilibrium constant

$$K_2 = \frac{[HCO_3^-].[H^+]}{[H_2CO_3]} = 4.687\times10^{-7}\ M$$

which yields the bicarbonate ion HCO_3^- ;and

$$HCO_3^- \longrightarrow CO_3^{2-} + H^+ \qquad (3)$$

which yields the carbonate ion, with equilibrium constant:

$$K_3 = \frac{[CO_3^{2-}].[H^+]}{[HCO_3^-]} = 4.687\times10^{-11}\ M$$

In pure water the equilibrium does not favour the formation of carbonate (CO_3^{2-}), or bicarbonate (HCO_3^-) ions and most of the CO_2 stays undissociated as hydrogen bicarbonate c.f. 'natural' rain water with a pH of 5.6 (see sulfur cycle). However in the oceans the excess hydrogen ions have over geological time scales reacted with basic minerals so that though the equilibrium expressions are still satisfied a large amount of carbon is dissolved as bicarbonate. Sea water has a pH of ~ 8 so that :

$$[HCO_3^-]_{rain}/[H_2CO_3]_{rain} = 1/6$$

$$HCO_3^-]_{rain}/[CO_3^{2-}]_{rain} = 53339$$

$$[HCO_3^-]_{sea}/[H_2CO_3]_{sea} = 43$$

$$[HCO_3^-]_{sea}/[CO_3^{2-}]_{sea} = 213$$

In natural rain water almost all of the carbon exists as hydrogen bicarbonate with only a small amount as bicarbonate and virtually nothing as carbonate, whereas

in the sea most resides as bicarbonate with a few percent as hydrogen bicarbonate and about half a percent as carbonate a small but significant amount. From these equations we can deduce the response of a well mixed layer to a change in the partial pressure of CO_2 by evaluating what is known as the buffering factor which tells us how much dissolved inorganic carbon (DIC) will increase for a given increase in atmospheric CO_2.

$$\xi = (\Delta(pCO_2)/pCO_2)/(\Delta DIC/DIC)$$

This buffer factor which can be easily determined from sea water typically has a value of ~10. This means that for a 10% increase in atmospheric CO_2 only a 1% rise in the total dissolved carbon is necessary to bring the system back to equilibrium. This has one very serious implication since it means that the oceanic reservoir behaves as if it were a reservoir $1/10^{th}$ of its apparent size. The buffer factor can be understood in the following terms. The bicarbonate ion is the most abundant ion in the sea. The bicarbonate concentration must be balanced against all the positive ions in the sea. These positive ions are present as a result of the weathering process washing minerals to the sea, in effect the bicarbonate ion is fixed on time scales of tens and hundreds of years by the concentration of positive ion. The sum of positive ions,excluding H^+ is known as the total alkalinity (TA).TA can only be change by the addition of positive ions,since TA is in secular steady state with the sources and sinks of positive ions,TA is effectivly fixed on time scales

shorter than geologic.Because TA is fixed any changes in bicarbonate concentration must be balanced by changes in hydrogen ion concentration i.e. changes in pH. At lower pH bicarbonate is less soluble and so any extra CO_2 trying to dissolve will find the effective solubility reduced (Baes,1982).

3.5 Calcium Carbonate.

There is one other important physical equilibrium which we need to consider if we wish to try and understand the carbon cycle. That is the equilibrium between calcium carbonate and its solvated ions.

$$CaCO_3 \quad \text{-->} \quad Ca^{2+} + CO_3^{2-}$$

This equilibrium depends on both temperature and pressure such that the crystalline form is favoured at lower pressures and higher temperatures. Near the surface of the oceans the crystalline form is most stable and decreases in stability as we go to deeper cooler water (see Fig 7).

The ocean receives various salts from runoff so let us explore the effects of the biological activity in the ocean on these salts. In order to grow living tissue a plankton must absorb carbon. The most abundant carbon species available to a sea creature is the bicarbonate ion HCO_3^-. This will be reduced in a reaction which we can represent by:

$$H^+ + HCO_3^- \rightarrow (H_2CO) + O_2$$

i.e. the biological activity tends to reduce the number of hydrogen ions and so reduce the pH of the solution. By considering the carbonate equilibrium we can show that the carbonate concentration is related to pH by the expression:

$$[CO_3^{2-}] = K_1K_2K_3pCO_2/[H^+]^2$$

i.e. reduced pH means reduced carbonate concentration and increased pH means increased carbonate concentration. As already mention positive ions are washed into the sea. One of these ions, calcium has an important part to play in the solution chemistry of the oceans. Because of the activity of the biota increases the pH of the sea , the increase in the product of calcium ion and carbonate ion concentration now greatly exceeds the value of the solubility product for these ions and the sea becomes supersaturated w.r.t. calcium carbonate.

3.6 The Rain of Detritus.

Why should this be important?When various plankton grow in the oceans the often form elaborate crystalline skeletons (called tests). Some of these tests are made of calcium carbonate. When the plankton die they sink. If there is sufficient oxygen their

organic material will be oxidized back to CO_2 and water. This will happen until the oxygen supply at that level has been used up. The calcium carbonate tests will not dissolve immediately, because the water will be supersaturated w.r.t calcium carbonate, but will continue to sink, as will any unoxidized organic carbon. The tests will continue to sink eventually reaching the lyocine (the level at which the ocean water become just saturated w.r.t calcium carbonate). Below the lyocine they now dissolve, thus achieving a nett transfer of carbonate to the deep ocean.This is often refered to as the 'rain of detritus'.

While this flux is very much smaller than the physical fluxes associated with the ocean upwelling and downwelling it is estimated to be large enough to balance the slightly greater flux from upwelling and produce a small nett transfer to the deep ocean. If we consider the areas of primary productivity in the oceans and the areas of upwelling,we find that these areas are spatially correlated.The upwelling nutriant rich water is rich in dissolved inorganic carbon which will be supersaturated w.r.t. surface pCO_2 and so in practise will be a nett source of CO_2.This correlation can be understood in the following terms.The deep ocean layers are associated with much higher levels of nutriants (phosphates and nitrates) which are necessary for the construction of proteins and other basic biological processes. The ratio of phosphate to nitrate is almost precisely the ratio found in living matter strongly hinting that the deep ocean reservoirs have

been enriched by the rain of detritis. Thus when deep waters upwell all the necessary nutriants to sustain growth are present in appropriate quantities and substantial growth is associated with the upwelling. Growth which will be highly correlated with the areas of upwelling and which will be instrumental in transfering carbon back to the deep reservoir. This would suggest that any increase in upwelling would be subject to some negative feed back.

Most of the carbon from these biological processes, which exists as carbonate in its fully oxidized state, will be in solution in the deep ocean, only where the deritus falls on surfaces above the lyocine will actual deposits of calcite (calcium carbonate) be laid down along with the organic carbon which we saw in an earlier lecture represents a nett flux of oxygen out of the oceans.

3.7 The Oxygen Cycle(Again?)

Because the deposition of reduced carbon is intimately linked with processes in the carbon cycle, a discussion of these processes has been deferred until now. From a knowledge of what biological material is composed of it is possible to deduce just how much oxygen would be required to oxidize a known amount of organic material it is also possible to deduce how much growth would be sustained if deep nutriant rich water were carried from the deep ocean to the surface layers it turns out that these processes are in detailed

balance. If pO_2 were to decrease ,more of the oceans would become anaerobic and less organic carbon would be oxidized contributing to an increase in O_2. Similarly if O_2 were to increase more of the oceans would become oxygenated so that more reduced carbon would be oxidized. The carbon that is not oxidized is layed down in sediments where it will eventually find its way back to the surface in natural geological processes and in fossil fuel combustion. Thus it should now be obvious that the regions of the oceans where these processes occur are very important to the future oxygen content of the atmosphere and it is the near surface layers which are crucial, i.e. the continental shelves,to both the oxygen and carbon cycles.

3.8 The Critical Zones.

Because of the dependence of calcite solubility on the levels of carbonate ion which in turn are, on short time scales, a function of partial pressure of CO_2 , increases in pCO_2 could undersaturate the surface layers w.r.t. calcite. If this were to happen then areas of the continental shelves where deposits of calcite are laid down would start to dissolve via the reaction:

$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3 + CO_2 + H_2O$$

this process would tend to take up more CO_2 and so feed back negativly on the CO_2. Current thinking suggests

that there will not be a significant sustained undersaturation w.r.t. calcite. However, it is believed that aragonite (a less stable crystal form of calcium carbonate) may suffer sustained undersaturation because of differences in the solubility of calcite and aragonite. The significance of this is that most coral is composed of aragonite and so could be vulnerable if CO_2 levels continue to rise. It would appear that there are several physical and chemical processes which would tend to stabilize increases in atmospheric CO_2. However it is likely that they would take at least several hundred years to establish new equilibria.

3.9 The Ultimate Control.

There is evidence which suggests that over geological time scales the CO_2 levels in the atmosphere have been gradually decreasing,from extemely high levels early in the history of the Earth to the pre industrial levels of 275 ppmv. This decrease in CO_2 has gone on at the same time as the luminosity of the Sun has been increasing. It has been suggested that this trend in solar heating has been far in excess of the trends which have been experienced in terrestial temperature (Fig 8) (Sagen& Mullen,1972). The mechanism which has influenced the atmospheric CO_2 is the weathering of certain rock types (mainly silicates and carbonates. Both of these react with CO_2, the reactions are:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$

$$2NaAlSiO_6 + 2CO_2 + 3H_2O \rightarrow 2Na^+ + 2HCO_3^- + AlSiO_5(OH)_4 + 4SiO_2$$

The rate at which this weathering takes place would appear to be governed by a simple physical process which depend on the partial pressure of CO_2. However if one considers the problem further we find that the pCO_2 levels found in soils are far in excess of the CO_2 in the atmosphere. This extra pCO_2 means that the rate of weathering in soils is much higher than would be predicted for abiotic weathering. This excess pCO_2 is maintained in the soils by microbal activity. The levels of CO_2 present are also found to be temperature dependent, higher temperatures , leading to higher levels of CO_2.This in turn leads to increased rates of weathering. Thus again we see that the biota have a significant role to play in the modulation of atmospheric gases.

3.10 Conclusions.

o Much of the regulation of the levels of atmospheric gases is controlled by marine processes on the time scales of immediate interest to mankind.

o The ultimate regulation of the CO_2 levels resides in the weathering of rock (carbonates and silicates). This process is enhanced and modulated by biological activity in the soil.

o Though the oceans could eventually take up all the excess CO_2 being produced this process would take thousands of years, thus we can reasonably expect CO_2 levels to continue to rise.

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Scope 29

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Science 177,p52-56

Fig 1.

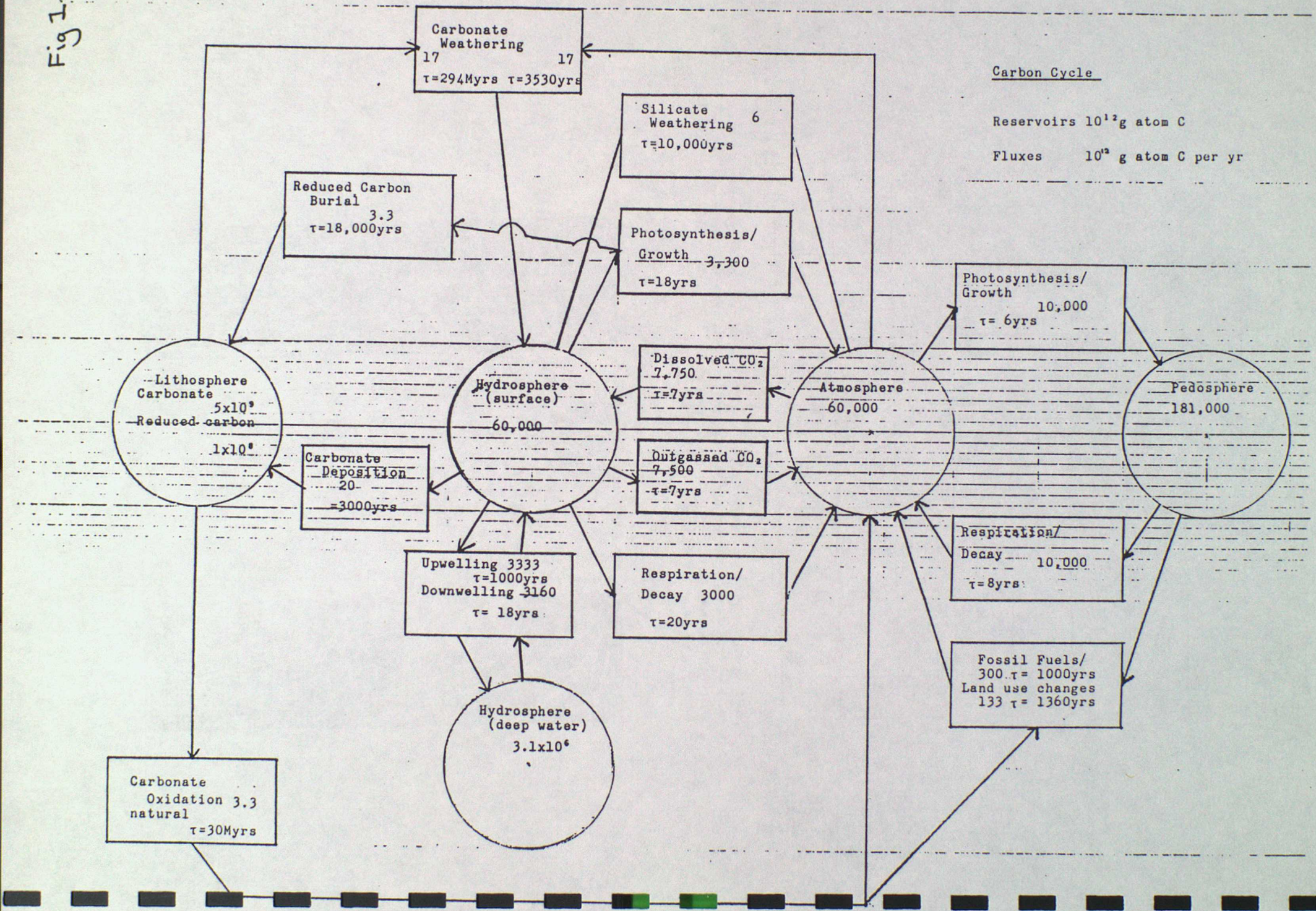
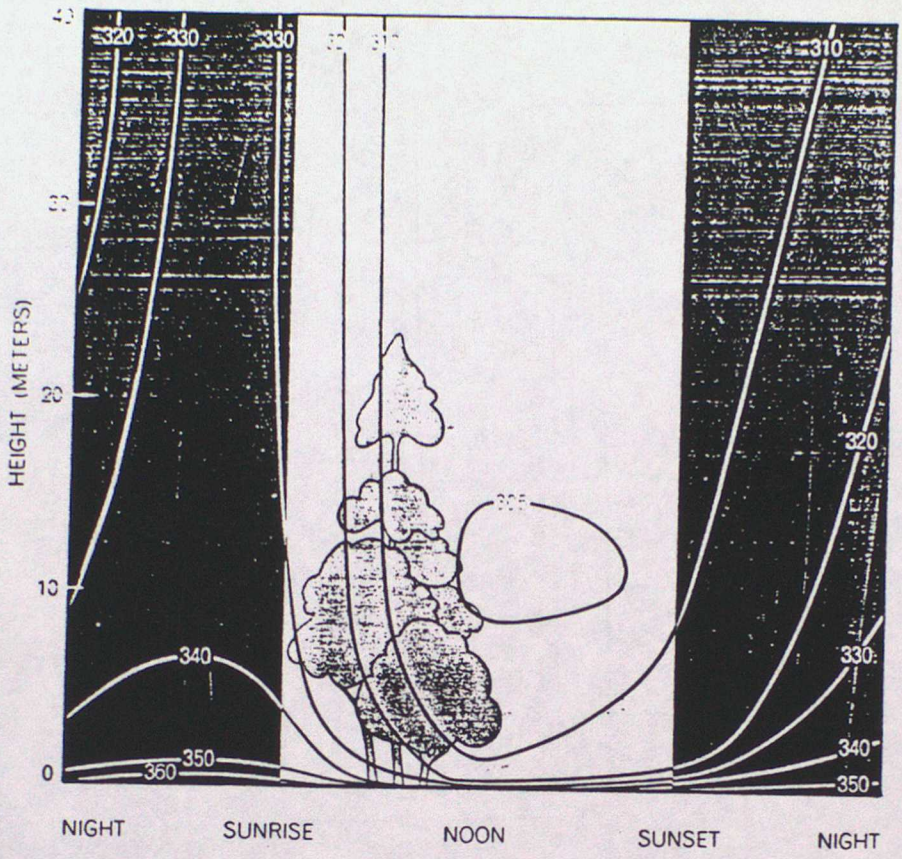
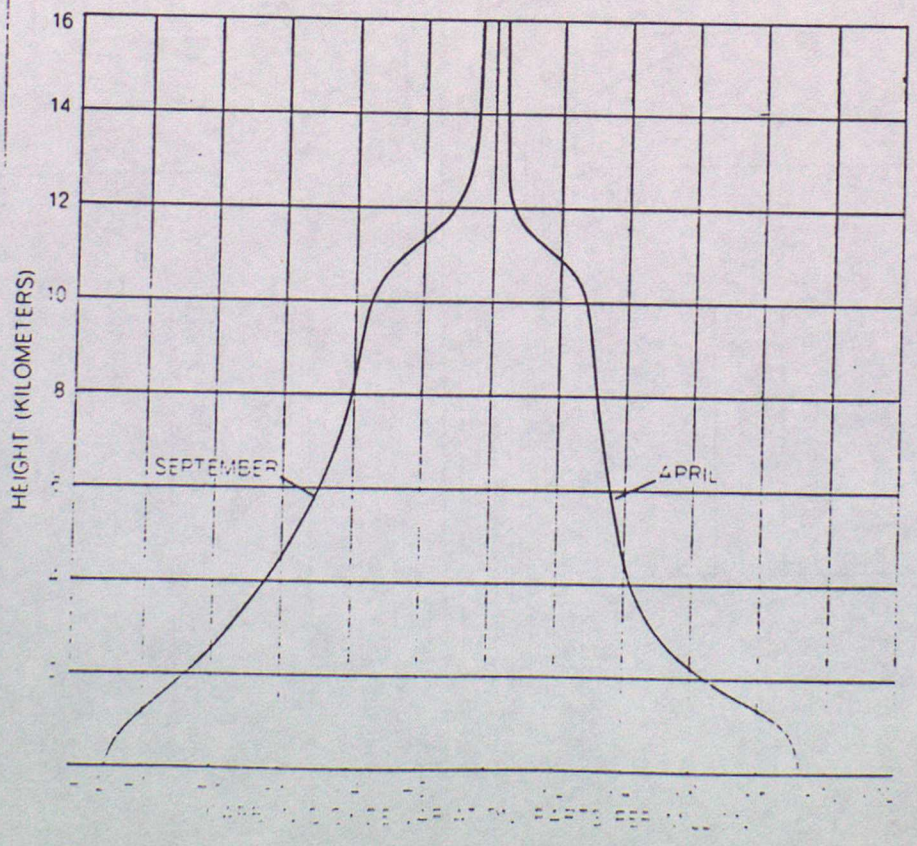

Carbonate Weathering
17 17
τ=294Myrs τ=3530yrs
Silicate Weathering 6
τ=10,000yrs
Reduced Carbon Burial
3.3
τ=18,000yrs
Photosynthesis/ Growth 3,300
τ=18yrs
Carbon Cycle
Reservoirs 10^{18}g atom C
Fluxes 10^{15} g atom C per yr
Photosynthesis/ Growth
10,000
τ= 6yrs
Lithosphere Carbonate
5x10⁹
Reduced carbon
1x10⁸
Hydrosphere (surface)
60,000
Dissolved CO₂
7,750
τ=7yrs
Atmosphere
60,000
Pedosphere
181,000
Carbonate Deposition
20
=3000yrs
Outgassed CO₂
7,500
τ=7yrs
Respiration/ Decay
10,000
τ=8yrs
Upwelling 3333
τ=1000yrs
Downwelling 3160
τ= 18yrs
Respiration/ Decay 3000
τ=20yrs
Fossil Fuels/
300 τ= 1000yrs
Land use changes
133 τ= 1360yrs
Hydrosphere (deep water)
3.1x10⁶
Carbonate Oxidation 3.3
natural
τ=30Myrs

Fig 2



VERTICAL DISTRIBUTION OF CARBON DIOXIDE in the air around a forest varies with time of day. At night, when photosynthesis is shut off, respiration from the soil can raise the carbon dioxide at ground level to as much as 400 parts per million (ppm). By noon, owing to photosynthetic uptake, the concentration at treetop level can drop to 305 ppm.

Fig 3



SEASONAL VARIATIONS in the carbon dioxide content of the atmosphere reach a maximum in September and April for the region north of 30 degrees north latitude. The departure from a mean value of about 320 ppm varies with altitude as shown by these two curves.

Fig 4

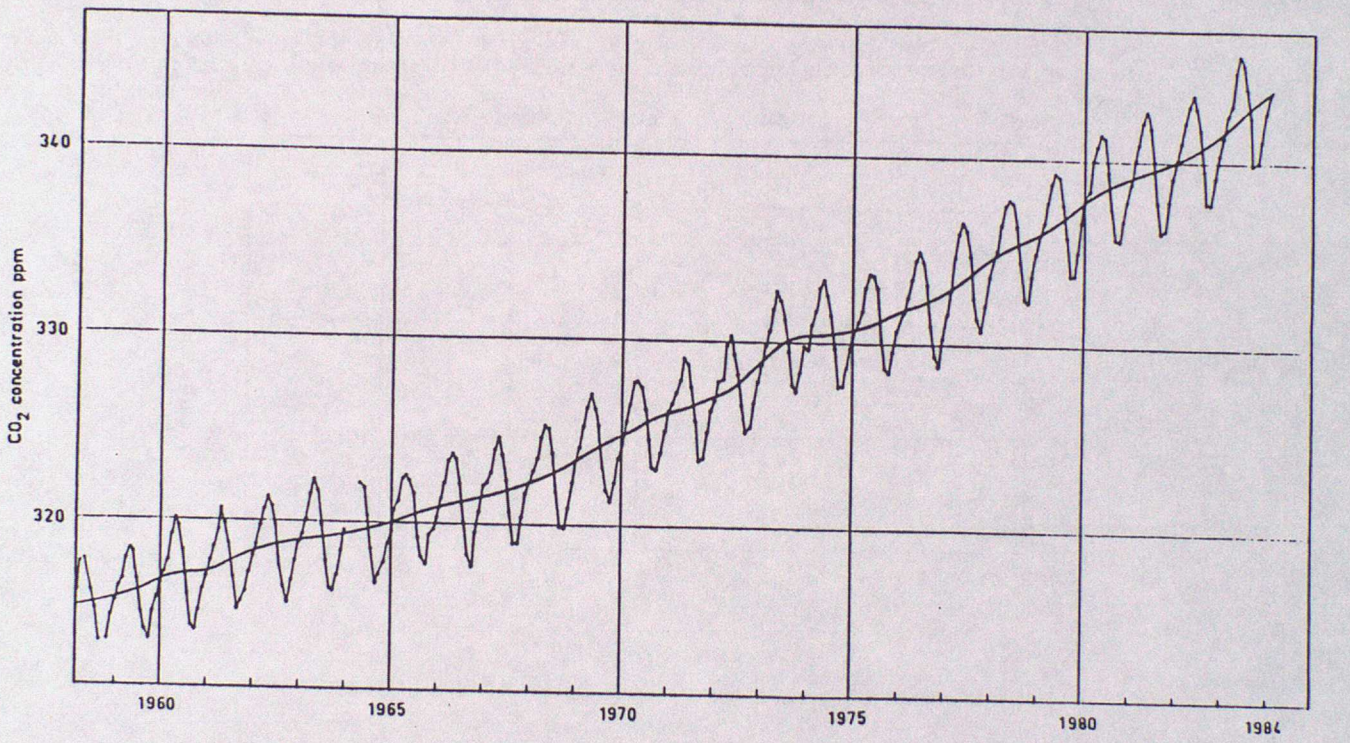


Figure 3.2 Concentration of atmospheric CO_2 at Mauna Loa Observatory, Hawaii. Dots indicate monthly averages determined from continuous measurements. Based on data reported by Bacastow and Keeling (1981), supplemented by data from recent years supplied by personal communication

Fig 6

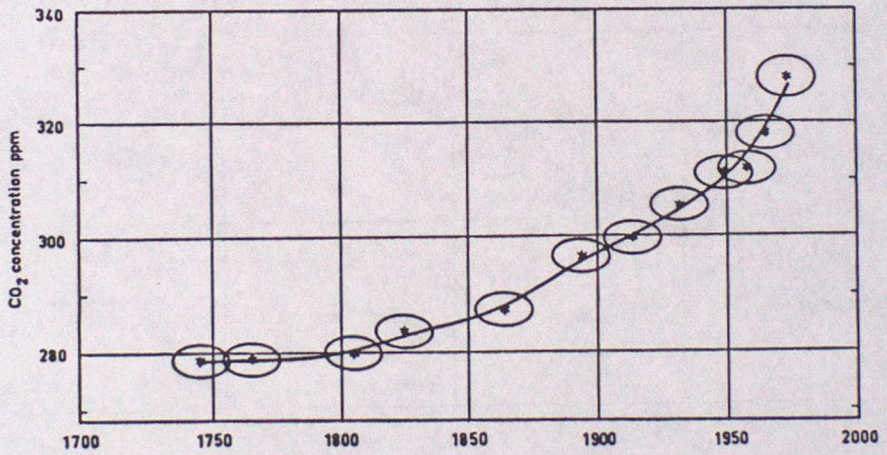
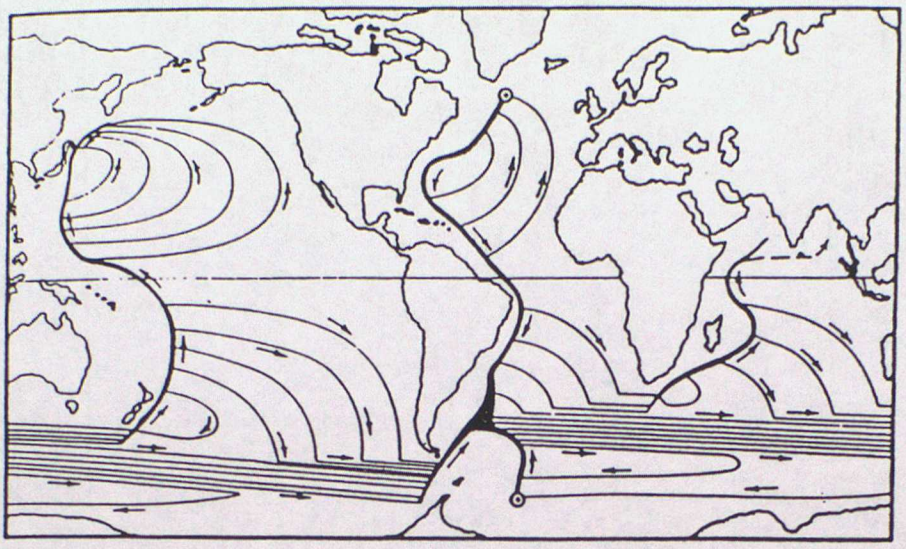


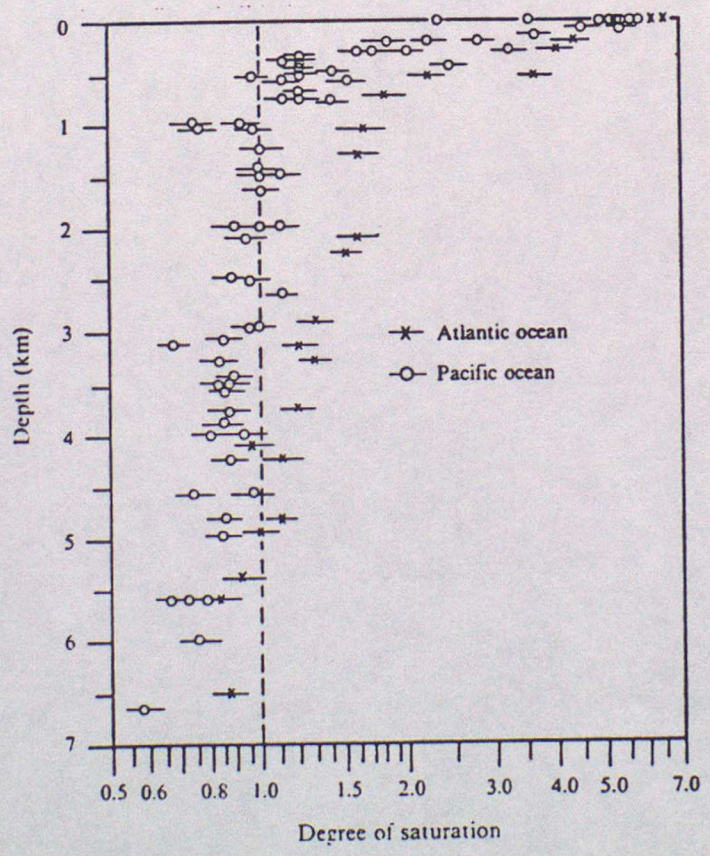
Figure 3.3 Atmospheric CO_2 concentrations measured in glacier ice formed during the last 200 years (Neftel *et al.*, 1985)

Fig 7



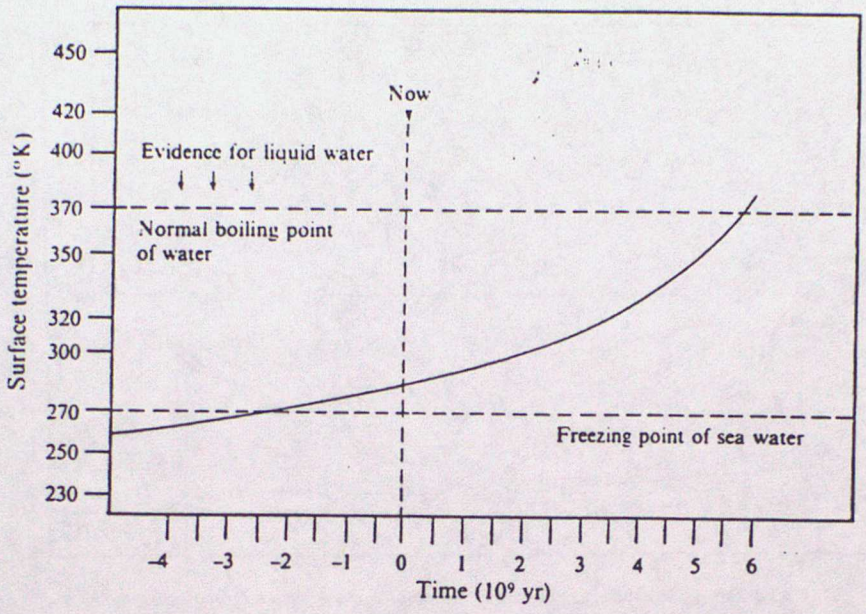
A schematic of the abyssal circulation of the world's ocean, driven by sources in the North and South Atlantic. If the two sources, ⊕, in the North and South Atlantic are taken as $20 \times 10^6\ m^3\ s^{-1}$ *each, then transport between the streamlines is of the order of* $5 \times 10^6\ m^3\ s^{-1}$. *(Reproduced from H. Stommel (1958),* Deep Sea Research, *5, 81, figure 1, with permission of Pergamon Press.)*

Fig 8



The degree of supersaturation of calcite in the Atlantic and Pacific oceans. (From L., Y.-H., Takahashi, T., and Broecker, W.S., Degree of saturation of $CaCO_3$ in the oceans. *J. Geophys. Res.* 74, 5507-5525, 1969. Copyrighted by American Geophysical Union.)

Fig 9



Evolution of the surface temperature of the earth assuming that the solar luminosity has increased, at a constant rate, by 30% since the origin of the solar system. The albedo has been taken to be 0.35, the emissivity of the surface to be 0.9, and atmospheric composition has been assumed invariant and equal to that of the present day. (After Sagan and Mullen, 1972.)

Lecture 4: Atmospheric Photochemistry

4.1 Introduction

Solar radiation not only heats the terrestrial atmosphere, it also drives much of chemistry through photochemically initiated processes. The subsequent effects of these primary photochemical reactions are then determined by the balance between large numbers of often competing chemical reactions. This lecture summarises the principles of photochemistry and the ensuing chemical reactions (gas kinetics), with examples relevant to the terrestrial atmosphere.

4.2 Photochemistry

Photochemistry in the earth's atmosphere is largely driven by solar radiation in the visible and ultra-violet wavelength regions of the electro-magnetic spectrum. The absorption of a photon with energy hv (h is Planck's constant and v is the frequency) will lead to electronic excitation of a molecule. This can be shown schematically as:

$$AB + h\nu \rightarrow AB^*$$

Where the * denotes excitation of the molecule AB. There are a large number of recognized fates for AB* in the earth's atmosphere (see Figure 1). Of main concern to us are dissociation and quenching.

A highly simplistic view of the bonding of atoms to form a molecule (assumed diatomic for further simplicity) consists of a potential well (Figure 2a)) in which the potential energy (PE) varies with the internuclear separation with a minimum at some equilibrium distance r_e. The nuclei are free to oscillate in the well and it can be shown that vibrational states occur with essentially uniform energy level spacing at low energies. The spacing tends to zero as the vibrational energy of the molecule approaches E_d. The molecules occupy these states according to a Boltzman distribution, lower energies being more highly populated. In practice, molecules have a number of such energy level systems, each associated with different electron configurations. Photons with energies corresponding to the separation of two states could, subject to selection rules, cause internal transitions. This gives rise to a series of discrete, uniformly spaced absorption features (Figure 2b). In practice, many rotational transitions would be associated with each vibrational transition (since $\Delta E_{vib} >> \Delta E_{rot}$). The net effect is a series of bands of vibration-rotation absorption lines corresponding to each vibrational transition. Once the photon energy exceeds E_d, the molecule is no longer bound - dissociation occurs - with any excess energy being removed as translational energy. Since there is essentially no constraint on the exact photon energy, a continuum absorption is now seen (Figure 2b)). This process is usually represented as

$$AB^* \rightarrow A + B^*$$

Quenching occurs when the excited molecule collides with a neighbouring molecule (usually N_2 or O_2 - referred to below as M) and reverts to its ground energy state, either transfering its energy or converting it to translational energy (heat):

$$AB^{*} + M \rightarrow AB + M^{*}$$

4.2.1 Radiation in the Earth's Atmosphere

The spectral distribution of solar radiation at the top of the atmosphere is shown in Figure 3 for different solar conditions (note the logarithmic irradiance scale). At very high photon energies there are large fluctuations depending on the degree of solar activity. At wavelengths longer than 100nm, emission from hydrogen in the Lyman α line represents an important source of energy.

As indicated in the first lecture, this spectrum is severely attenuated by passage through the atmosphere (Figure 4). At short wavelengths the principal absorbers are O_2 and O_3.

4.2.1.1 Molecular oxygen

Even the simplest molecules have a complex potential energy curve structure. For O_2, the most significant transitions in the atmosphere are the $B^3\Sigma^-_u \leftarrow X^3\Sigma^-_g$ band and the weak (formally forbidden) $A^3\Sigma^+_u \leftarrow X^3\Sigma^-_g$ band (Figure 5). The $B^3\Sigma^-_u \leftarrow X^3\Sigma^-_g$ transition gives rise to the Schumann Runge bands between 175 and 200nm (Figure 6) while at shorter wavelengths (higher energies) dissociation occurs in the Schumann Runge continuum yielding one ground state and one excited oxygen atom (Figure 7). Transition to an unbound (repulsive) state can also occur giving rise to two ground state oxygen atoms (so called predissociation). At still shorter wavelengths the O_2 absorption is still high, but with a hundredfold decrease in the absorption cross-section in the vicinity of the Lyman α solar emission line. This coincidence allows deep atmospheric penetration of Lyman α radiation.

Between 150nm and 242nm is the Herzberg continuum ($A^3\Sigma^+_u \leftarrow X^3\Sigma^-_g$). This band is formally forbidden by selection rules, but is important because of the high solar energies in this region of the spectrum. The net O_2 absorption is shown in Figure 8.

As well as attenuating the incoming solar flux, dissociation of O_2 is an important source of atomic oxygen.

4.2.1.2 Ozone

The primary absorption of ozone occurs in the Hartley band (200-310nm). In this region photon energies are sufficiently high to produce excited atomic oxygen atoms. Weaker O_3 absorption bands occur at longer wavelengths - the Huggins bands (310-350nm) and the Chappuis bands (500-800nm) - see Figure 9. O_3 absorption and dissociation in the Huggins and Chappuis bands is the main source of atomic oxygen atoms in the low stratosphere and troposphere and is important in initiating much photochemistry in those regions.

The net effect of these two absorbers is shown in Figure 10 in terms of the altitude corresponding to a 1/e attenuation of the radiation at the top of the atmosphere. At wavelengths longer than 310nm, the atmosphere is optically thin (has high transmission) and solar radiation penetrates to the surface, with little dependence on the solar zenith angle. The O_3 Hartley and O_2 Herzberg bands result in peak radiation absorption around the stratopause and the Schumann Runge bands and continuum cause absorption mostly in the thermosphere. As the atmosphere is strongly absorbing at wavelengths <310nm, the radiation flux at these wavelengths reaching a given level will depend strongly on the solar zenith angle. (The absorber amount with a zenith angle of 90° is ≈70

times that in a vertical column: the transmission is thus $\tau_{vert}^{2.5}$). Also, in spectral regions dominated by O_3 absorptions, the solar flux will depend on the ozone column, which varies by a factor of ≈2 depending on latitude and season.

4.2.2 Scattering of Radiation

Even in the cloud free atmosphere the solar radiation flux is modified by scattering. At wavelengths shorter than 4000nm this scattering is due only to air molecules and Rayleigh theory may be applied. This gives rise to a wavelength dependence for scattering proportional to λ^{-4}. The effects of this scattering on the solar flux are shown in Figures 11a) and b). Figure 11a) shows the atmospheric attenuation in various spectral regions with no scattering - radiation at wavelengths longer than 310nm reaches the ground without significant attenuation while radiation at shorter wavelengths is absorbed in the upper atmosphere. Once multiple scattering is included (Figure 10b)), the radiation flux at longer wavelengths is *increased* substantially, exceeding the downward flux at the top of the atmosphere by factors approaching 2. Effects are most marked at longer wavelengths where atmospheric attenuation is small, but significant effects are visible at ≈305nm. The inclusion of a ground (or cloud) albedo of 0.5 increases the radiation flux further (Figure 11c)). Enhancement factors in excess of 2 are seen at wavelengths longer than 320nm. When modelling photolysis rates, the inclusion of scattering and appropriate ground/cloud albedos are particularly important for molecules which can absorb solar photons

at wavelengths longer than ≈300nm. These include molecules such as O_3, NO_2, NO_3, N_2O_5, HOCl and $ClONO_2$.

The rate of photodissociation of a molecule in the atmosphere is determined by a convolution of the absorption cross-section of that molecule with the radiation field produced by O_2 and O_3 absorptions and scattering and albedo effects acting on the incoming solar flux. In certain instances the photons may not be sufficiently energetic to cause dissociation and the excited molecule is rapidly quenched. This constraint is incorporated in the form of a quantum yield.

4.3 Gas Kinetics

As two molecules approach the potential energy of the composite rises (Figure 12). If the orientation of the molecules is favourable and their translational energy is large enough, they will continue to approach until their potential energy (PE) ceases to rise. Once this point is reached the reactants rapidly fall into the PE well with the resultant products (AB,C) being formed. The amount of energy released by the reaction is ΔH. For energetically favourable (exothermic) reactions ΔH is negative. For an endothermic reaction (ΔH positive) to proceed, the reactants must possess internal exitation at least as large as ΔH. The presence of a PE barrier means that most two body reactions have a positive temperature dependence (slower at colder temperatures).

While in principle it is possible to compute the rate of a reaction given the barrier energy curve (or more usually energy surface), in

practice it is not yet possible except for the simplest reactions. Recourse is made to experimental measurement. Given the Boltzman distribution of thermal energies of reactants and the potential barrier, it is not suprising that experimentally derived reaction rates follow the form:

$$k = Ae^{-E/kT} \quad (\text{molec cm}^{-3}\text{s}^{-1})$$

where A, the pre-exponential and E, the activation energy are experimentally derived.

The rate of the reaction P+Q→R+S would then be given by the law of mass action, viz k.[P].[Q] where [] denotes the concentration of that constituent in number density per unit volume.

Reactions involving 3 constituents generally do not occur in a single collision, but in a succession of closely spaced bimolecular reactions, the final being quenching of an excited product (this must occur before it dissociates back to its component reactants). A schematic example would be

$$A + B \rightarrow C^* \qquad k_1$$

followed by

$$C^* + M \rightarrow C + M^* \qquad k_2$$

which can be reversed by the unimolecular (thermal) decay

$$C^* \rightarrow A + B \qquad k_3$$

At high temperatures k_3 will proceed more rapidly (and k_2 less rapidly slowing the net rate of reaction. This gives rise to a negative temperature dependence (*faster* at colder temperatures). The net effect of reactions k_1-k_3 are generally written

$$A + B + M \rightarrow C + M$$

with, as for a bimolecular reaction, empirically derived rates and temperature dependences.

4.4 Ozone Formation

Given the basic photochemical processes, how is O_3 formed? Chapman first proposed an oxygen only scheme for stratospheric O_3. The initial step was the photolysis of O_2:

$$O_2 + h\nu \rightarrow O + O \qquad J_1$$

followed by rapid recombination of the atomic oxygen in a three body reaction:

$$O + O_2 + M \rightarrow O_3 + M \qquad k_4$$

Rapid photolysis of O_3:

$$O_3 + h\nu \rightarrow O_2 + O \qquad J_2$$

followed by recombination (k_4) leads to a rapid photochemical equilibrium between O and O_3, the ratio O/O_3 being a rapidly changing function of altitude (smaller at higher pressures).

Recombination:

$$O + O_3 \rightarrow O_2 + O_2 \qquad k5$$

is the major oxygen only sink. In the Chapman scheme, 'odd oxygen' - i.e. $[O]+[O_3]$ is produced (slowly) by J_1, destroyed (slowly) by k_5, while the O/O_3 ratio is maintained throughout by k_4 and J_2.

Studies of the ozone photochemical balance showed that in the stratosphere, model calculations using chemistry based on oxygen alone yielded ozone concentrations approximately twice those observed. Other chemical destruction mechanisms apparently must exist. In 1950, Bates and Nicolet postulated the existence of *catalytic cycles* involving hydrogen oxides as additional O_3 sinks. Since then additional cycles

involving nitrogen oxides (Crutzen, 1970) and chlorine oxides (Rowland and Molina, 1975) have been identified.

Catalytic cycles overcome the problem of how molecules present at mixing ratios of ppbv or less can influence O_3 which is present in the middle stratosphere at mixing ratios of ≈10ppmv.

A schematic catalytic destruction cycle would be:

$$X + O_3 \rightarrow XO + O_2 \qquad k_6$$

$$\underline{XO + O \rightarrow X + O_2} \qquad k_7$$

$$\text{net:} \quad O + O_3 \rightarrow O_2 + O_2$$

Remembering that the balance between O and O_3 is maintained, the destruction of O is equivalent to destroying O_3. The significant part of this cycle is that X is regenerated. X thus determines the *rate* of ozone destruction, not the absolute amount. In the earth's atmosphere X could be OH, NO, Cl or Br.

The existence of OH and NO in the atmosphere depends on the presence of excited atomic oxygen $O(^1D)$ produced either by O_3 photolysis at $\lambda<310$nm or by O_2 photolysis at $\lambda<175$nm. Much of the $O(^1D)$ is quenched, but some molecules collide with H_2O:

$$H_2O + O(^1D) \rightarrow OH + OH$$

or with N_2O:

$$N_2O + O(^1D) \rightarrow NO + NO$$

Chlorine oxides are produced in the stratosphere largely by the breakdown of man-made CFCs, natural methyl chloride or methyl chloroform. Bromine oxides, though not yet observed in the stratosphere are thought to be present from anthropogenic halogen emission and subsequent stratospheric breakdown.

The relative effectiveness of the different destruction cycles depends on the relative abundances of the catalysts (determined in part by reservoir gases - see below), and on the reaction rates which are strongly temperature dependent. In Figure 13 are shown the computed relative importance of the destruction mechanisms at various levels in today's atmosphere. Below 20km in the stratosphere, the X=NO cycle becomes less important and with depleted levels of O a different catalytic cycle, involving the reactions:

$$X + O_3 \rightarrow XO + O_2 \qquad k_6$$

$$\underline{XO + O_3 \rightarrow X + O_2 + O_2} \qquad k_8$$

$$\text{net:} \quad O_3 + O_3 \rightarrow O_2 + O_2 + O_2$$

with X=OH becomes the principal destruction mechanism for O_3.

4.5 Reservoir Gases

Up to this point we have thought of the different O_3 destruction mechanisms as being independent, their effects linearly additive. In fact, this is far from being the case. There are many reactions which in some cases link different reaction chains which form in many cases long lived (hours, days) molecules which tie up otherwise reactive molecules and atoms. The formation of these so called reservoir gases, which may then be transported to other locations before dissociation, has a profound effect on the ozone destroying potential of an air mass.

The principal stratospheric reservoir gases are shown below (other gases - e.g. peroxyacetyl nitrate ($CH_3COO_2NO_2$, PAN) are important in the troposphere).

Reservoir	Formation	Destruction	Lifetime
*HNO_3	NO_2+OH	OH, hv	days/weeks
HNO_4	NO_2+HO_2	OH, M, hv	<1 day
N_2O_5	$NO_2+O_3 \rightarrow NO_3+O_2$ then NO_2+NO_3	M, hv	<1 day
$ClONO_2$	$ClO+NO_2$	M, hv	<1 hour
*HCl	$Cl+CH_4$	OH, O, hv	days/weeks
HOCl	$ClO+HO_2$	OH, hv	<1 hour
*H_2O_2	HO_2+HO_2	OH, hv	<1 day

M denotes thermal decomposition and * indicates reservoirs which are soluble and can thus act as net sinks if washed out. Certain reservoirs tie up several molecules of one chemical family, others link two different families. Of these reservoirs, HNO_3 has been measured on numerous occasions including from satellites. HCl has been observed on a limited number of occasions from balloons and satellites. Several measurements now exist for $ClONO_2$ and there is strong evidence for presence of HNO_4 and N_2O_5. However, the existence of HOCl and H_2O_2 have not been confirmed by measurements although an upper limit for the latter exists. The diurnal variations of $ClONO_2$, N_2O_5 and HNO_4 have yet to be observed. Lack of knowledge concerning reservoirs represents one of the major areas of uncertainty in our understanding of photochemical processes in the atmosphere.

4.6 Tropospheric Photochemistry

While O_3 in the stratosphere shields the surface from harmful UV radiation, direct contact with high concentrations of tropospheric O_3 is known to have detrimental effects on plant growth and animal health. However, the photochemical regime in the troposphere differs from that

in the stratosphere - for example there is very little atomic oxygen in the tropcsphere, and different catalytic cycles dominate. In the presence of CO (or many hydrocarbons) the following catalytic cycle operates:

$$CO + OH \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$\underline{HO_2 + O_3 \rightarrow OH + O_2 + O_2}$$

net: $$CO + O_3 \rightarrow CO_2 + O_2$$

CO is oxidised to CO_2 with a net loss of one O_3 molecule, but with no change in OH. However, in the presence of sufficient NO (absolute value uncertain, but ≈20pptv (parts per 10^{12}) a different cycle operates and HO_2 formed in the second reaction now reacts with NO rather than O_3:

$$CO + OH \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$\underline{O + O_2 + M \rightarrow O_3 + M}$$

net: $$CO + 2O_2 \rightarrow CO_2 + O_3$$

In this case there is a net *production* of one molecule of O_3. There are equivalent (but more complex) chains in which hydrocarbons are oxidised ultimately to CO_2 which may produce not only O_3, but also OH and HO_2 which then accelerate further O_3 production. Many aspects of even the simplest of these chemical reaction chains are untested.

4.7 Uncertainties

The above discussion gives the impression that our understanding, at least of stratospheric photochemistry is relatively complete. In very broad terms this may be true. However, even in the regions of the atmosphere thought to be photochemically controlled andwell understood, for example in the upper stratosphere at low latitudes there are significant discrepancies between observed O_3 mixing ratios and those calculated in 1 and 2 d numerical models (Figure 14). In part this may represent deficiencies in the averaging inherent in the 1 and 2 d approaches (see lectures 8 and 9), but there are indications that hydrogen oxide chemistry is the weakest link in our knowledge. There are very few measurements of OH in the upper stratosphere, no direct measurements in the low stratosphere or free troposphere, and where measurements of both OH and HO_2 exist (above 30km), their ratio, an exceedingly simple calculation in current photochemical models, is in error by a *factor of 30*. This indicates profound problems with either measurement technique or model assumptions (or, of course, both).

The importance of atomic oxygen in O_3 destruction has been made clear above and indeed the ratio of O/O_3 is a basic prediction by models - yet only one simultaneous measurement of the O and O_3 profiles exists and doubts have been expressed over the O_3 results.

Very recent papers suggest that the O_2 and O_3 absorption cross-sections require further refining, leading to changes in the solar fluxes calculated by models.

One area which has yet to be seriously approached is that of reactions taking place on surfaces - heterogeneous reactions. Many

reactions which are very slow in the gas phase may occur rapidly on surfaces - e.g. cloud particles or aerosol, or in solution. Laboratory measurement of heterogeneous reaction rates are particularly difficult - a serious problem in view of the empirical approach to gas kinetics currently in use.

Perhaps the most worrying indication that our understanding of atmospheric photochemistry is incomplete are the substantial (≈50%) ozone reductions recently observed over Antarctica. These were not predicted and are yet to be satisfactorily explained. These depletions (though not the explanation!) are the subject of another lecture.

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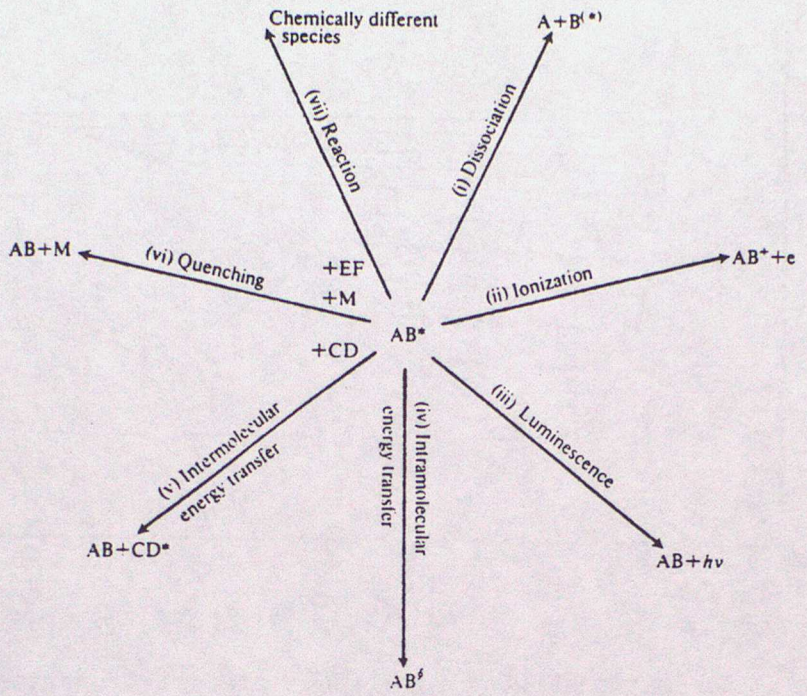

Figure 1 Pathways for loss of electronic excitation that are important in atmospheric chemistry. Those of main interest to us are dissociation and quenching.

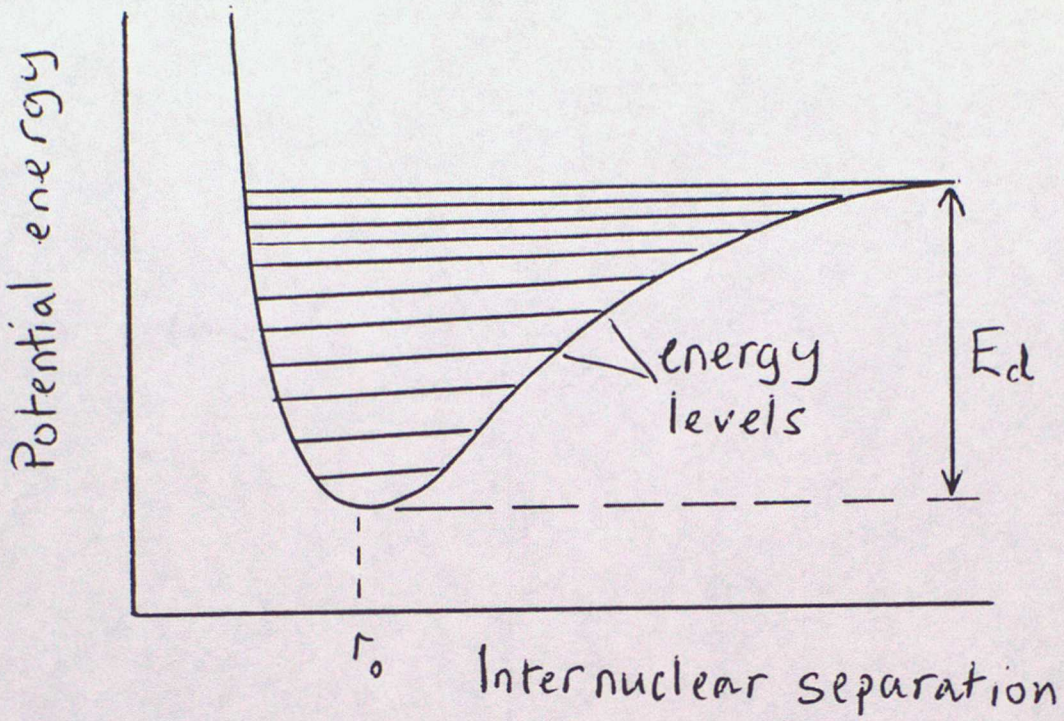

Figure 2a) Schematic showing idealised molecular potential energy curves and energy level structure. E_d is the energy necessary for dissociation from the ground state. The energy level separation diminishes as this limit approaches.

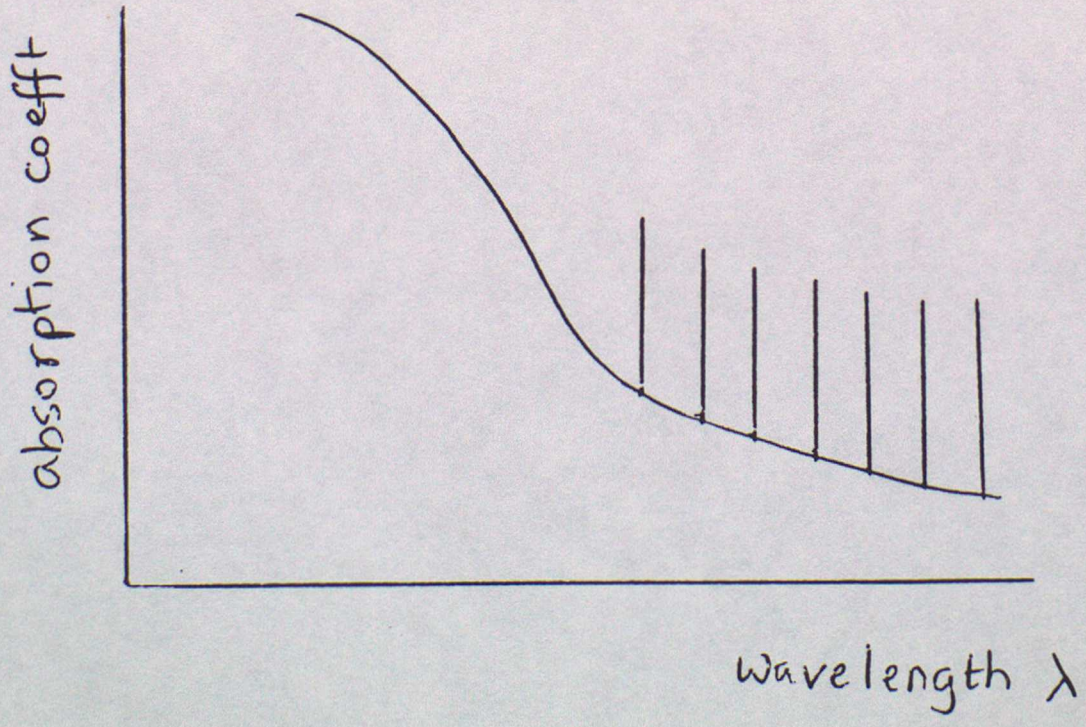

Figure 2b) Schematic showing the absorption coefficient associated with different photon wavelengths. At long wavelengths the molecule does not dissociate and a banded absorption structure is observed. At shorter wavelengths the molecule does dissociate and a continuum results.

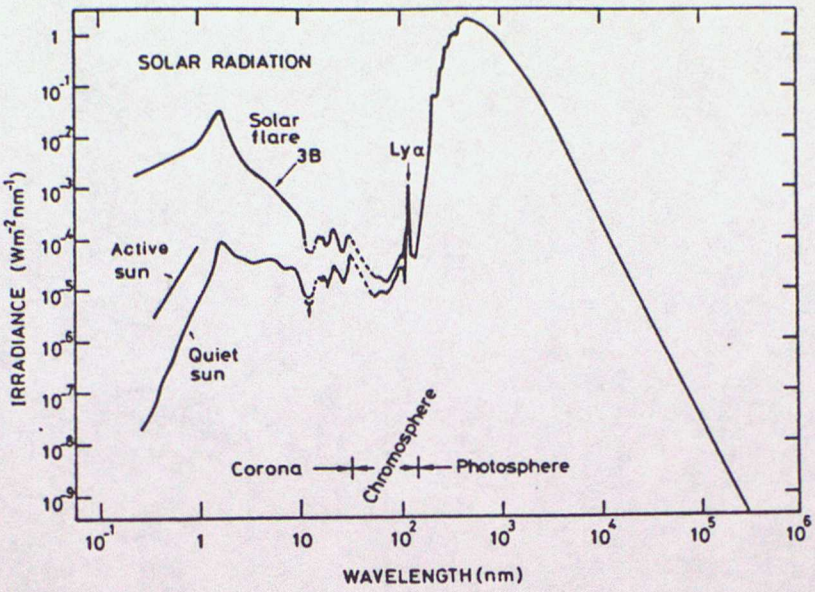

Figure 3 The spectral distribution of solar irradiance and its variation with solar activity. Note the logarithmic scale.

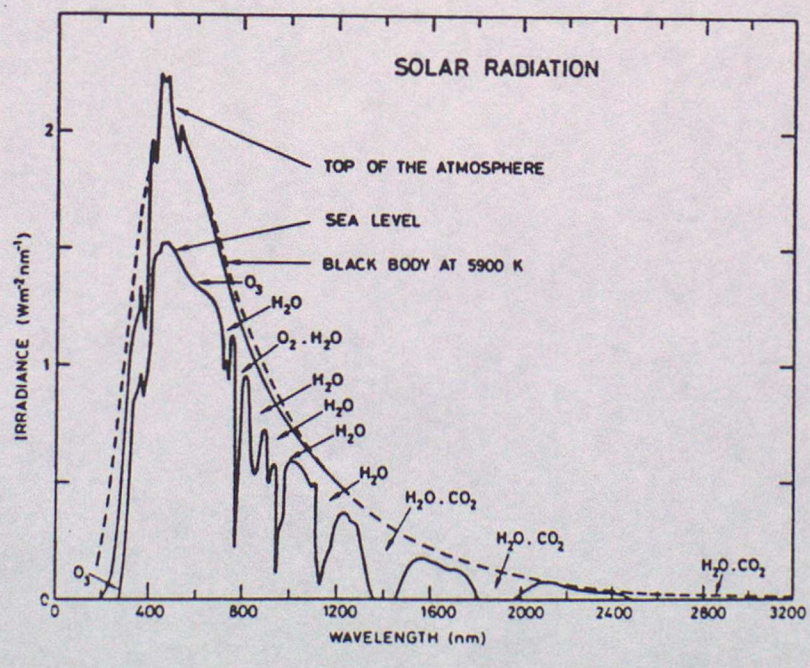

Figure 4 The spectrum of solar radiation (UV, visible, IR) outside the earth's atmosphere and at the surface, showing the principal absorbers.

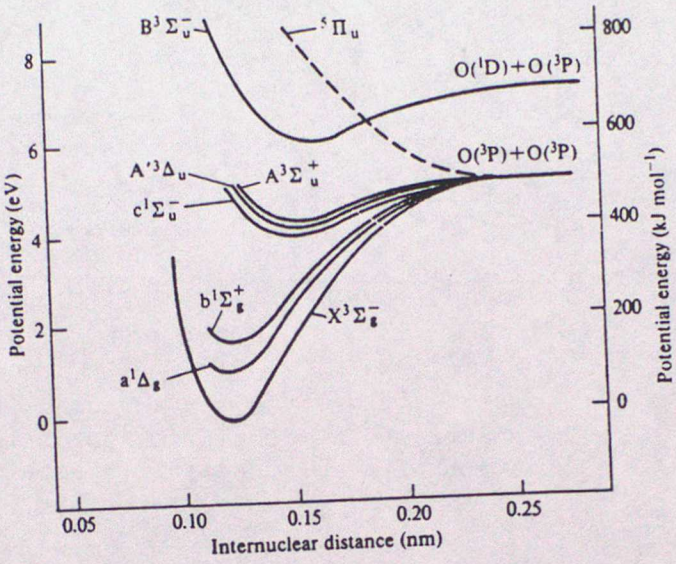

Figure 5 Potential energy curves for some of the states of molecular oxygen. The ground state is labelled X, the main excited states A and B. Those who want to know what the symbols denote should refer to Herzberg (1950). The dashed curve is a repulsive state which can lead to dissociation of an otherwise bound excited state (transition to this stae is termed predissociation).

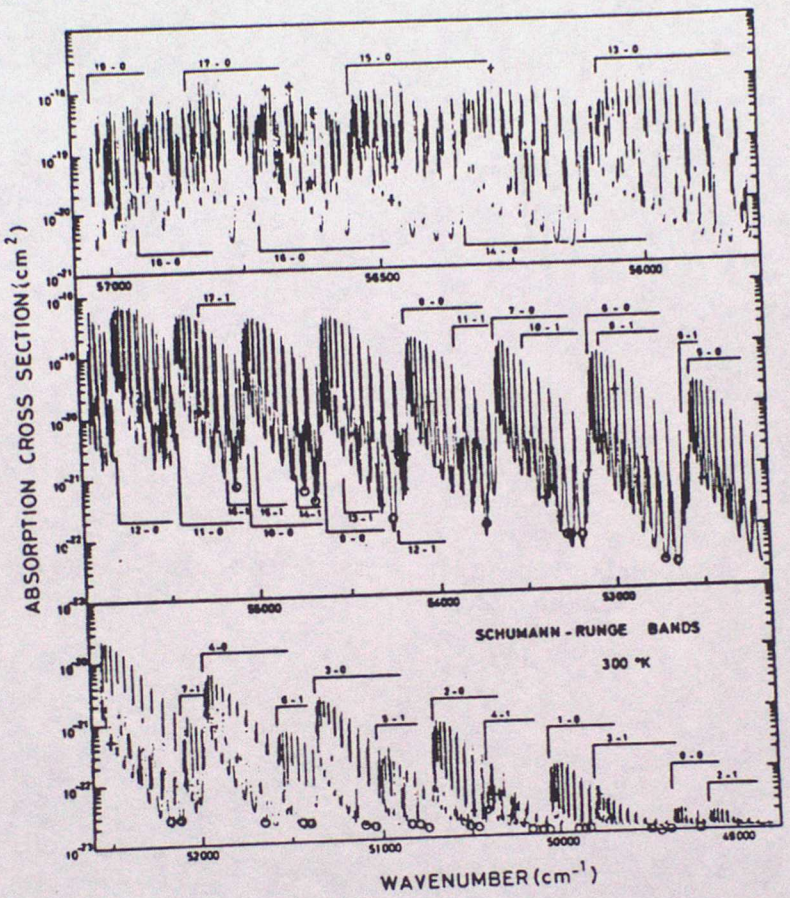

Figure 6 Spectral distribution of the absorption cross-section of molecular oxygen in the Schumann Runge bands ($B^3\Sigma^-_u \leftarrow X^3\Sigma^-_g$) . Note the fine structure associated with rotational transitions.

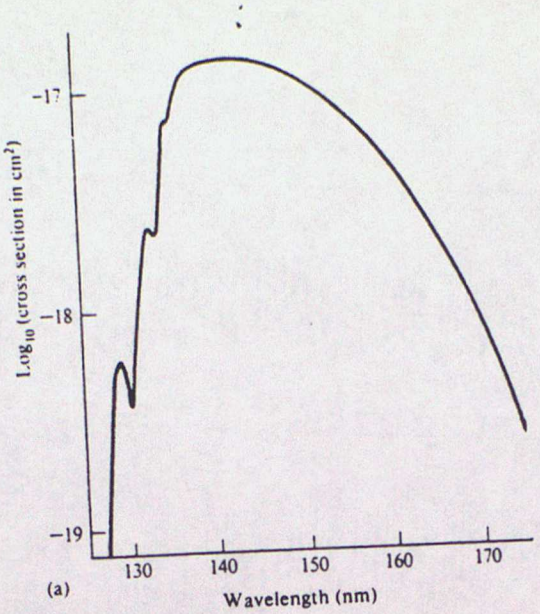

Figure 7 Absorption spectrum of molecular oxygen in the $B^3\Sigma^-_u \leftarrow X^3\Sigma^-_g$ Schumann Runge continuum.

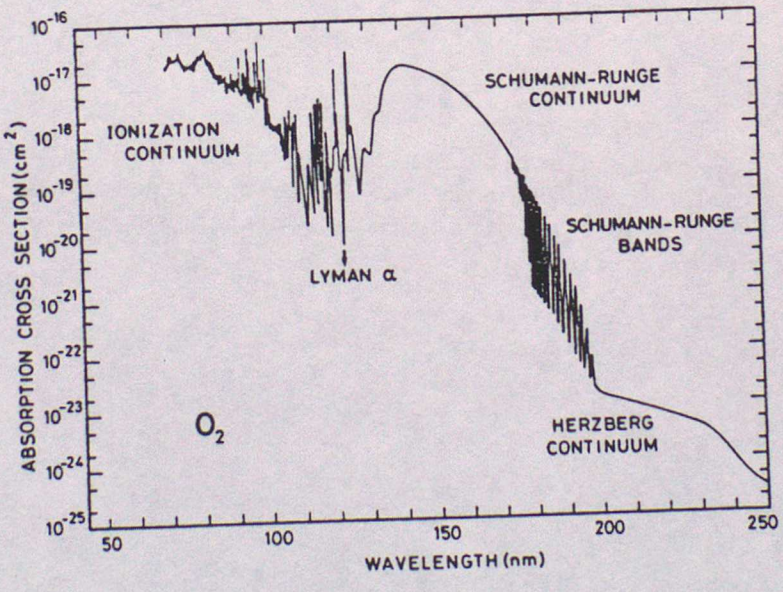

Figure 8 Spectral distribution of the net absorption cross-section of molecular oxygen.

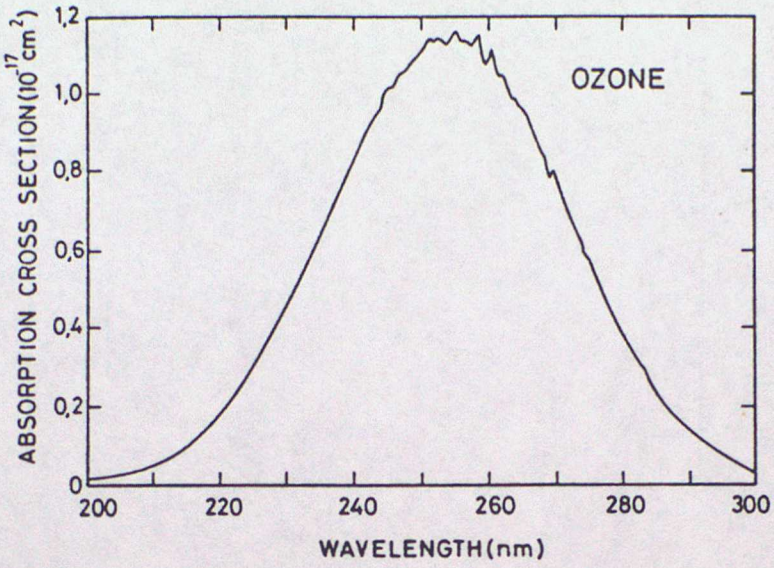

Figure 9a) The Hartley band of ozone.

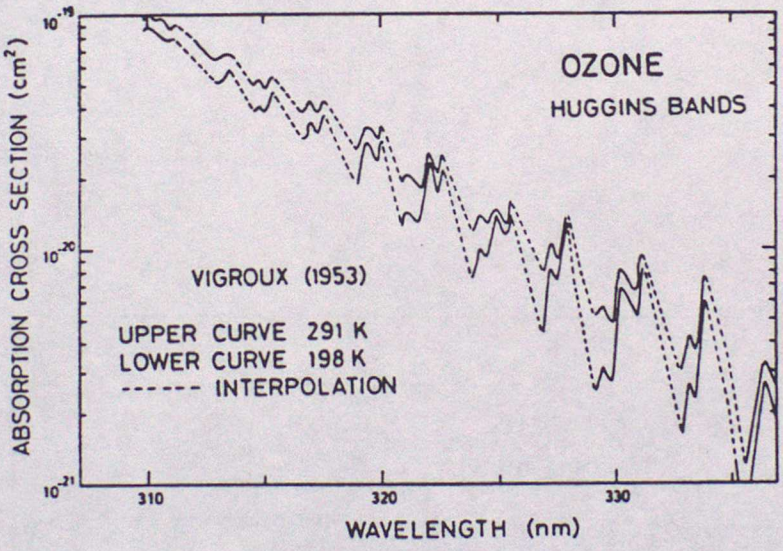

Figure 9b) The Huggins bands of ozone. The absorption in these bands has a pronounced temperature dependence.

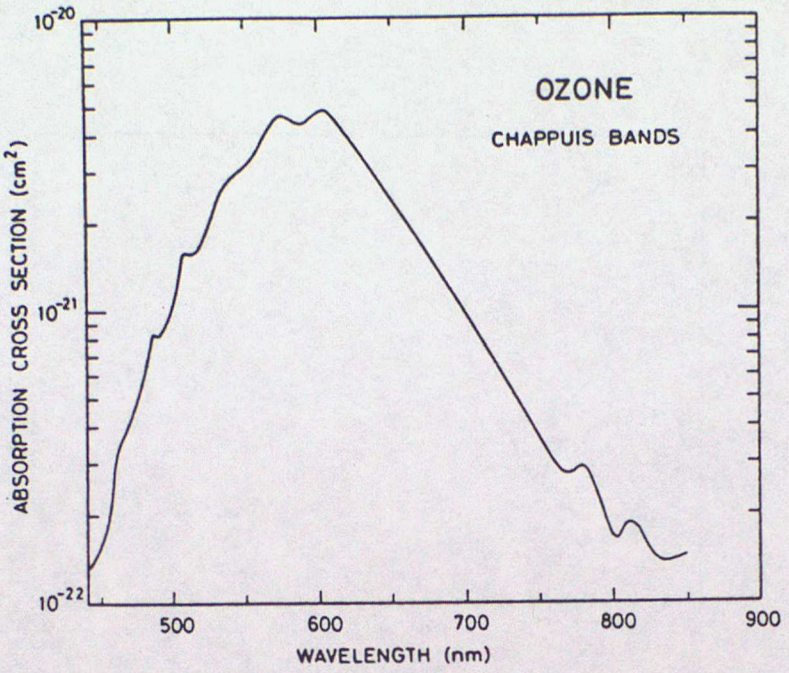

Figure 9c) The Chappuis bands of ozone.

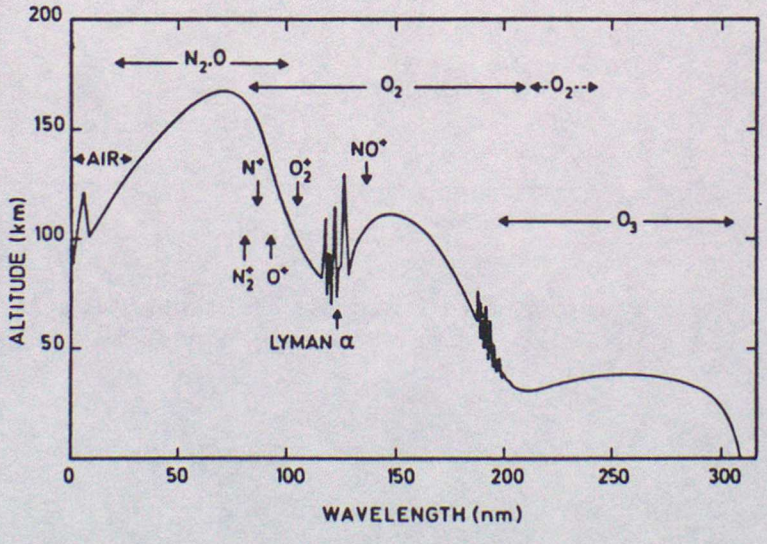

Figure 10 Depth of penetration of solar radiation at different wavelengths. Altitudes correspond to 1/e attenuation.

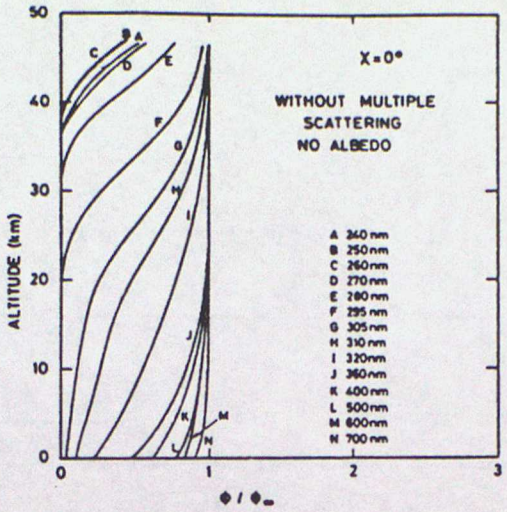

Figure 11a) Attenuation of solar radiation with altitude at different wavelengths shown in terms of an enhancement factor. In this case only absorption is considered.

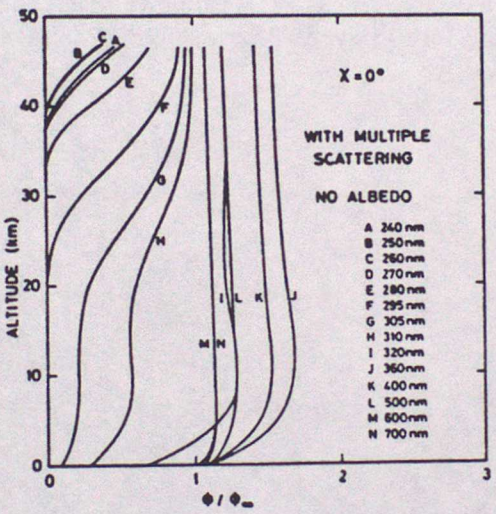

Figure 11b) As Figure 11a) except the effects of multiple scattering are included.

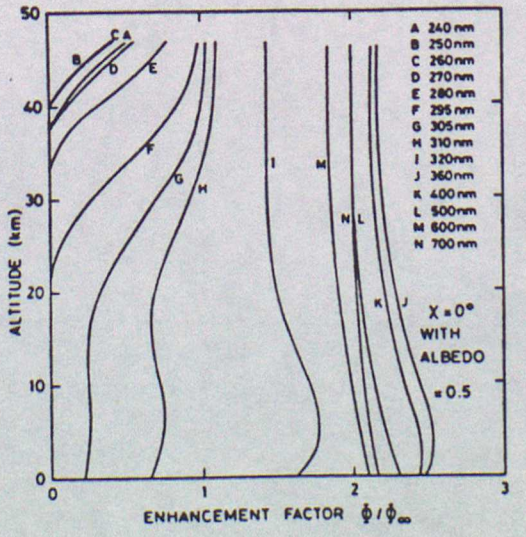

Figure 11c) As Figure 11b) except the effects of a ground albedo of 0.5 are also included.

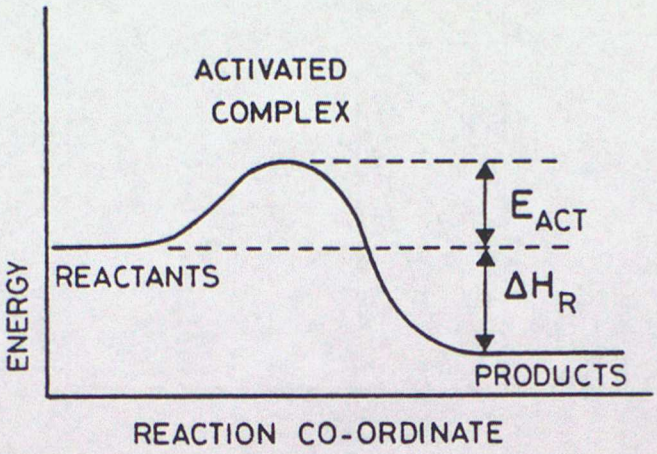

Figure 12 Reactant energy (enthalpy) as a function of 'reaction coordinate' (intermolecular distance). The reactants must possess energy in excess of E_{ACT} if the reaction is to proceed.

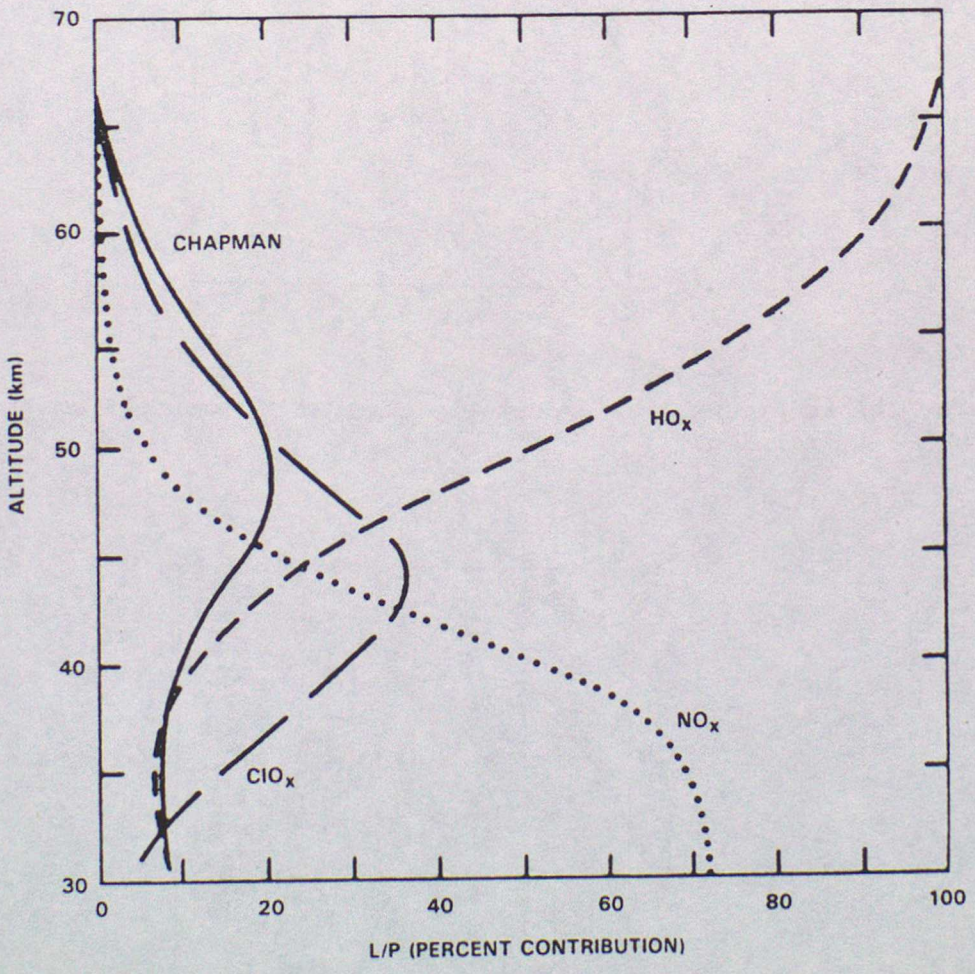

Figure 13 Ratio (%) of the odd oxygen ($O+O_3$) loss rate due to the Chapman, hydrogen oxide, nitrogen oxide and chlorine oxide catalytic destruction mechanisms as a function of altitude. L and P are the net loss and production rates respectively.

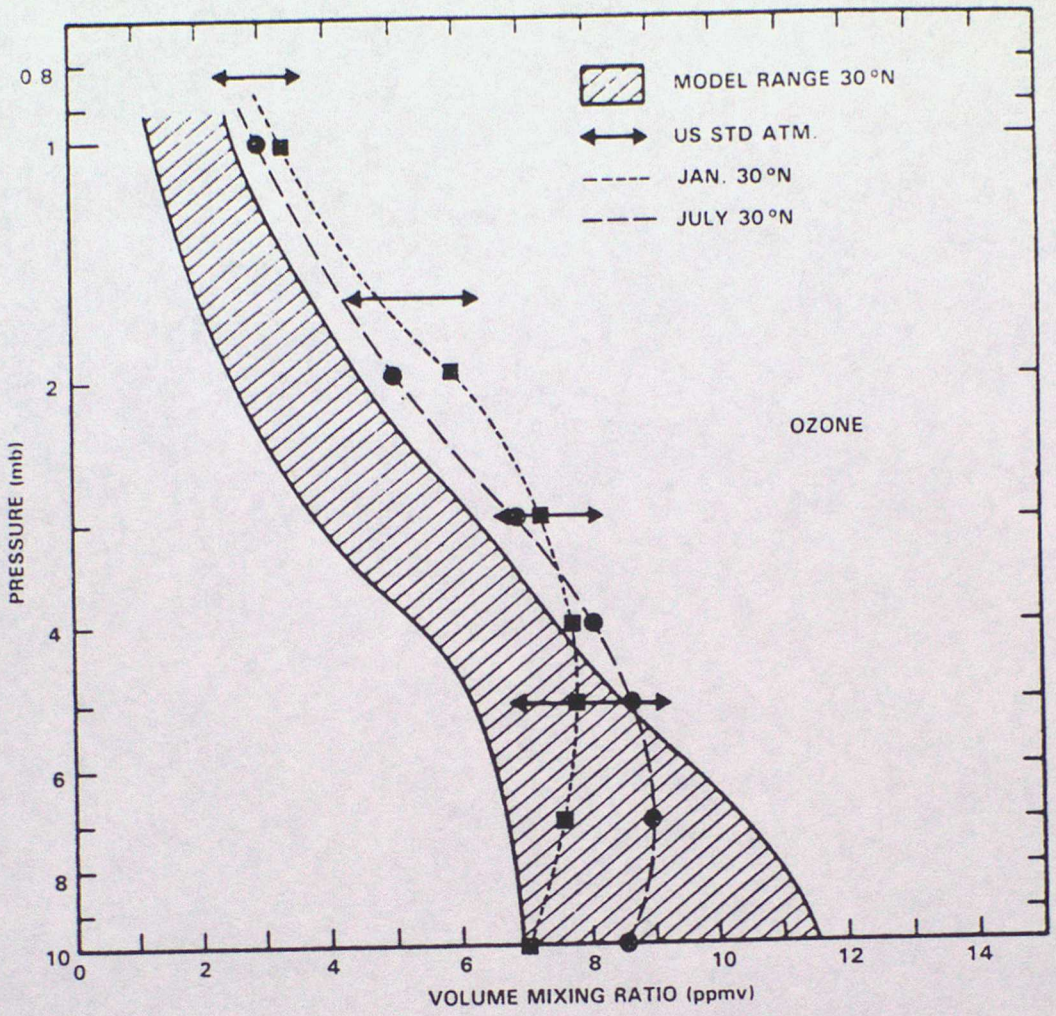

Figure 14 Vertical distribution of O_3 in the upper stratosphere. The dashed curves are representative profiles for 30°N. The shaded region includes summer and winter 2 d model calculations for 30°N. The models and observations diverge above ≈5mb.

Lecture 5: Upper Atmospheric Chemistry

5.1 Observations and Model Predictions of Ozone Change

In the preceding lectures we have described some of the fundamental processes which are responsible for determining the chemical state of the atmosphere. Over the last decade or more, these processes have been modelled with increasing sophistication in order to predict the effects of man's activity on the atmosphere and particularly on ozone in both the troposphere and the stratosphere. Among the main recognised threats to the stratospheric ozone layer are the halocarbons, notably the CFCs 11 and 12 ($CFCl_3$ and CF_2Cl_2) whose atmospheric concentrations are currently increasing at around 5% per year. It has also been recognized that concurrent changes in other gas concentrations - e.g. CO_2, CH_4 and N_2O, both through direct chemical means and indirectly via atmospheric temperature changes unfluencing temperature dependent chemistry, must be considered.

One stringent test of any model used to predict change is the extent to which it simulates the present state of the atmosphere. Some unresolved deficiencies in the modelling of current upper stratospheric ozone concentrations have been commented on previously. Another test would be to model the changes which have ocurred over the last two decades, a period over which reactive chlorine in the atmosphere is thought to have approximately doubled. In Figure 1 are shown latitude-height cross-sections of predicted O_3 differences between 1965 and 1985.

The model used assumed that only reactive chlorine had changed over the period (from 1.3ppbv in 1965 to 2.7ppbv in 1985). Solstice and equinox sections of ΔO_3 are shown. Concurrent increases in CO_2 or CH_4 would tend to mitigate the modelled depletions. The broad picture is of depletions of ≈10% in the mid latitude upper stratosphere with larger depletions (20-30%) at high latitudes. The increased depletion at high latitudes arises because the concentration of CH_4 (whose source is in the troposphere and which is gradually destroyed in the stratosphere) is lower at high latitudes in the stratosphere. The lower CH_4 mixing ratios slow the reaction

$$CH_4 + Cl \rightarrow HCl + CH_3$$

This has the effect of reducing the amount of Cl and ClO held in the reservoir HCl, increasing the rate of O_3 destruction by the chlorine (X=Cl) catalytic destruction cycle. In the low stratosphere, regions of O_3 enhancement are seen. This is because a reduction in O_3 in the upper stratosphere allows more short wavelength radiation to penetrate to the lower stratosphere, increasing the source of O_3 by photodissociating more O_2. Despite the relatively large percentage changes at upper levels, the net changes in O_3 column 1965-85 are very small (<1%) even at high latitudes.

Over this period column ozone has been measured worldwide (well nearly) using a network of Dobson spectrophotometers. These instruments use a differential absorption technique which involves making atmospheric absorption measurements at pairs of closely spaced wavelengths in the UV which have different O_3 absorptions but similar scattering properties. The effects of scattering can thus be largely removed. In Figure 2 are shown measurements of column O_3 since 1958

'averaged' from 54°S to 75°N derived from the Dobson network data. Seasonal variations have been removed by a statistical method. There are negative anomalies apparent in 1983 (El Chichon erupted in this period) and again in 1986. In both cases there was a rapid recovery. Any long term trends estimated from these data would clearly depend on the sample period. Calculations show that the 1958-84 trend is downward, but is not statistically significant at the 5% level (-0.26±0.92%/decade). Other approaches using slightly shorter sample periods show somewhat larger, but still not statistically significant trends (-0.70±0.82%/decade). A major limitation in these analyses is that there are only 36 Dobson stations with sufficiently long records to be used in the analyses, and of these only 6 were in the Southern Hemisphere with 54°S being the southernmost latitude.

Studies of the vertical profile of O_3 have used the Umkehr Method. This is a system which relies on sunlight being scattered from different atmospheric levels as the sun rises or sets to achieve its vertical discrimination. In Figure 3 are shown the O_3 trends deduced using the Umkehr Method (13 stations only) at various levels in the stratosphere over the period 1970-80. In the upper stratosphere statistically significant depletions are apparent, consistent with model predictions at these latitudes.

Satellite borne instruments which in principle can provide complete global coverage suffer from calibration drifts which prevent trends either in the column or in the vertical profile of the magnitudes predicted by models from being detected reliably. A drift is clearly visible in Figure 2b) which shows globally averaged column O_3 from the

SBUV instrument since late 1978. Taken alone the satellite data would imply a significant downward trend.

5.2 The Ozone Hole

Until recently the broad consistency between model predictions and observations - despite some areas of discrepancy and certain untested aspects - provided sufficient justification for concluding that current models could usefully predict future trends, at least in broad terms. Recent observations of column ozone over Antarctica have cast serious doubt on this assertion. In Figure 4 are shown October mean values of column O_3 above Halley Bay (76°S) from 1957-84. Values have fallen from >300 D.U. (Dobson units - 1 D.U. corresponds to a column of ozone 10^{-3}cm high at STP) prior to 1970 to well below 200 D.U. by 1984. The Halley Bay data show that this depletion apparently builds up in September and October, with a recovery in November as the winter circulation breaks down (Figure 5). Satellite observations from the Total Ozone Mapping Spectrometer (TOMS) instrument on Nimbus 7 (launched in late 1978) has shown that this depletion extends over the entire vortex, with a minimum value in 1985 of 152 D.U., a reduction over historical values of ≈50%. For such a major reduction to have occurred, O_3 must have been removed from the *low* stratosphere where its abundance is high. Indeed, balloonsonde measurements from Syowa station and McMurdo Base (both 78°S) show that the depletion is *restricted* to the low stratosphere below ≈20mb, ≈27km (Figure 6). No major depletion occurred prior to the late 1970s. Model calculations have entirely failed to predict any depletion in this region, and on this timescale. At present the

depletion appears to be restricted to the Antarctic region (with possibly some indications of a similar, though smaller depletion in the Arctic). However, a key question is what the implications of this depletion are for global ozone: the climate change calculations mentioned in lecture 1 assumed column O_3 changes of a few % over the next 50 years. Before this question can be answered, the mechanism responsible for the reduction must be understood.

5.2.1 Possible Chemical Explanations of the Ozone Hole

It is useful first to consider why models failed to predict an ozone depletion. There are several reasons. Firstly, since the O/O_3 ratio is very small in the low stratosphere (Figure 7), standard catalytic ozone destruction cycles are very slow (lecture 4). Secondly, the concentrations of the reservoir gases (H_2O_2, HCl, HNO_3, N_2O_5, $ClONO_2$) are all calculated to be large in the low stratosphere so that the concentrations of reactive molecules (e.g. X and XO in the catalytic cycles) are anyway small. Indeed, models calculated the photochemical lifetime of O_3 to be hundreds of days at these times and locations.

Any chemically based hypothesis must therefore overcome three hurdles:

1) it must explain the trend,

2) it must overcome the unfavourable partitioning of reactive/reservoir gases predicted by standard chemistry,

and 3) it must incorporate a catalytic destruction mechanism which can operate efficiently in the low stratosphere.

Virtually all of the chemical hypotheses appeal to the steady increase in atmospheric chlorine via CFC release as the cause of the trend. One hypothesis suggests that nitrogen oxides produced by increased solar activity is responsible.

The paper which first identified the depletion suggested that, while nitrogen oxide chemistry was the dominant O_3 sink mechanism in the low stratosphere, its effect could be modulated by the addition of chlorine via photolysis of CFCs, and in the low temperatures found in the Antarctic vortex, additional chlorine would alter the NO/NO_2 ratio to make the nitrogen oxide O_3 destruction cycle more effective. By this means they were able to destroy significant O_3 amounts above 30km on a suitable timescale (4-6 weeks), but the destruction was not sufficiently fast in the very low stratosphere.

A number of workers have suggested that chemical reactions take place on the clouds frequently found in the low stratosphere at these latitudes during the late winter and early spring (polar stratospheric clouds - PSCs). The existence of reactions of this kind (heterogeneous reactions) has been postulated elsewhere in the stratosphere (Northern Hemisphere polar night) to explain increases in HNO_3 (see reaction h6 below). In this case heterogeneous reactions are thought to convert reservoir gases into more reactive forms. The main supposed reactions are

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3 \qquad h1$$

and $$H_2O + ClONO_2 \rightarrow HOCl + HNO_3 \qquad h2$$

these are then followed by either

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad J3$$

or $$HOCl + h\nu \rightarrow OH + Cl \qquad J4$$

The net effects of these reactions (1+3 or 2+4) are to release OH and Cl atoms from H_2O, $ClONO_2$ and HCl. These atoms then take part in the O_3 destroying reaction chains discussed below. In the presence of significant amounts of NO_2 (anticipated by conventional chemistry), the reaction:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad r5$$

will occur, reforming the reservoir $ClONO_2$ and depleting the reactive chlorine. To prevent this occuring, a third heterogeneous reaction is usually proposed:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad h6$$

Since N_2O_5 is formed from two NO_2 molecules (see lecture 4) this would tie up sufficient NO_2 to prevent r5 occuring at a significant rate. Reactions h1 and h2 have been observed in kinetic studies, albeit in physical conditions very different from those encountered with PSCs.

The inefficiency of the standard catalytic O_3 destruction cycles has been overcome in a variety of ways: given the enhanced OH and Cl produced by h1 and h2, one suggested route (Solomon et al., 1986) is that the reactions r7 and r8 rapidly occur. These are the initial reactions of the standard catalytic cycles. To overcome the absence of atomic oxygen O the reaction r9 then occurs, followed by J10.

$OH + O_3 \rightarrow HO_2 + O_2$ r7

$Cl + O_3 \rightarrow ClO + O_2$ r8

$HO_2 + ClO \rightarrow HOCl + O_2$ r9 cycle I

$\underline{HOCl + h\nu \rightarrow OH + Cl}$ (visible) J10

net (7-10) $2O_3 \rightarrow 3O_2$

The net effect is the destruction of 2 O_3 molecules.

Another reaction chain involves Br instead of OH (McElroy et al., 1986) viz:

$Br + O_3 \rightarrow BrO + O_2$ r11

$Cl + O_3 \rightarrow ClO + O_2$ r12 cycle II

$\underline{BrO + ClO \rightarrow Br + Cl + O_2}$ r13

net $2O_3 \rightarrow 3O_2$

and there is a ClO self reaction chain (Molina and Molina, 1987):

$ClO + ClO + M \rightarrow Cl_2O_2 + M$ r14

$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$ J15

$ClOO + M \rightarrow Cl + O_2$ r16 cycle III

$\underline{2Cl + 2O_3 \rightarrow 2ClO + 2O_2}$ r17

again with net $2O_3 \rightarrow 3O_2$

Cycle III has potential advantages in that as it is quadratic in ClO, it would produce a more pronounced depletion in O_3 for a given ClO trend. However, cycle III must also compete with thermal dissociation of Cl_2O_2 and the formation of OClO via

$Cl_2O_2 + h\nu \rightarrow OClO + Cl$ J18

followed by $OClO + h\nu \rightarrow ClO + O$ J19

both of which yield no net O_3 destruction. Cycle II is highly uncertain since the BrO concentration is unknown (there is a measured upper limit of 7-14pptv).

Crutzen and Arnold (1986) suggested that all nitrogen oxides are converted to HNO_3 (via h6) which is then removed onto PSCs. Even without other heterogeneous reactions, it is suggested that this would greatly enhance OH concentrations since the major OH sink in the stratosphere is by reaction with HNO_3. The enhanced OH would then liberate reactive chlorine from HCl and a cycle similar to I would operate.

One hypothesis which differs fundamentally from those described above is that *high* levels of nitrogen oxides produced in the mesosphere and thermosphere especially during periods of high solar activity around solar maximum (around 1980) are transported to the low stratosphere (Callis and Natarajan,1986). There is evidence that in the Northern Hemisphere nitrogen oxides are transported down to the *upper* stratosphere (above 40km) in the polar night region. The authors argue that this downward transport would be more effective in the more isolated Antarctic vortex. If the above is true, the hole might be expected to vanish as the solar minimum is approached.

Model calculations have incorporated these various schemes. For example, in Figure 8 is shown the number density of ClO as a function of altitude with, and without the heterogeneous reaction h1. In the model h1 is treated as being equivalent to a standard two body gas phase reaction, but with an enhanced rate. A substantial enhancement of ClO is seen in the low stratosphere. In Figure 9 is shown the net O_3 depletion arising from schemes I, II and III assuming an increase in atmospheric bromine and chlorine of 15-30pptv and 1-2.7ppbv respectively (the

chlorine increase is appropriate for the period 1958-85, the bromine increase is unknown and probably overestimated in the model). The model reproduces at least qualitatively most features of the observed depletion, although the magnitude of the modelled depletion underestimates that observed. However, many aspects of the chemistry are at best untested and at worst tuned to produce the depletion. The agreement between model and observations does not prove any of the hypotheses and may be entirely fortuitous.

5.2.2 Dynamical Theories of the Ozone Hole

On the basis that the area integral of column O_3 between 44°S and 90°S apparently remains unchanged during the depletion (Figure 10), a number of purely dynamical theories of the ozone hole have been put forward suggesting that dynamical redistribution rather than chemical destruction is taking place. These rely on the fact that the Antarctic vortex almost reaches radiative equilibrium by late winter. Radiative heating in the low stratosphere through the absorption of solar radiation by either clouds (PSCs) or aerosols as sunlight returns in early spring could, it is argued, lead to net upward motion within the vortex. Since the O_3 mixing ratio decreases with decreasing altitude, upward motion would transport air which is relatively poor in O_3 in to the lower stratosphere thus reducing the column. No rapid O_3 chemistry would be required. The trend in O_3 could be explained in a number of ways. Aerosol in the low stratosphere has increased in recent years mainly through volcanic activity (Figure 11), leading to increased heating and hence upwelling. Another suggestion is that the vortex is

now colder and hence longer lived than in the late 1970s. PSCs now exist for longer (it is argued) resulting in increased heating and upwelling in recent years.

5.2.3 Observations in Antarctica

It is almost certainly premature to talk of observations of chemical composition within the vortex bearing in mind that a number of measurement campaigns will be in progress by the time this lecture is given. However, in 1986, measurements made from McMurdo Base (78°S) from late August to late October revealed that the chemistry appeared to be highly perturbed in the low stratosphere. Being somewhat selective, measurements showed that:

1) the NO_2 column was *lower* within the vortex than recorded anywhere else on earth.

2) column OClO measurements were higher than ever recorded elsewhere.

3) measurements in the μwave are consistent with ClO mixing ratios in the low stratosphere as high as 1-2ppbv. If correct, this implies almost complete conversion of CFCs to reactive chlorine.

4) the N_2O column was *lower* than model predictions.

The implications of 1)-3) are that while the ozone destroying potential of the various chains is unknown at low stratospheric temperatures (e.g. the relative importance of J18 to J15), the chemical composition and notably the partitioning between reactive and reservoir species appears strongly perturbed. The low NO_2 values (point 1)) are not consistent with the solar cycle related hypothesis. There are some indications that

the O_3 depletion continues after the surfaces assumed necessary for heterogeneous reactions (the PSCs) have vanished. Work performed within the Office has shown that temperatures in the low stratosphere in September have not changed over a period in which O_3 column amounts have halved. This, and 4) above argue against hypotheses involving upwelling (which would draw N_2O rich air into the low stratosphere.

Changes in sea surface temperatures (SST) have been monitored since the last century. Since the late 1950s when O_3 measurements were available in Antarctica, SST changes in the Southern Hemisphere have shown a very good correlation ($r=-0.67$, significant at the 1% level) with the October mean column O_3 measurements made from Halley Bay (Figure 12). While this correlation is not understood, one interpretation is that the circulation, driven by SSTs, is exerting some control over the depth of the depletion.

As yet, no conclusive identification of the depletion mechanism is available.

Global Implications

The global significance of what at present appears to be a localized phenomenon is of much concern. One recent work has suggested that similar, although less marked depletions are evident in satellite (SBUV) ozone observations in the Northern Hemisphere. Large corrections for instrument calibration drifts have been applied to these data (±0.4%/year). The global trends computed from these data are approximately an order of magnitude greater than those from Dobson network data, admittedly over a shorter period. The data show the

Antarctic depletion (-5%/year in October) and a depleted region in the Northern Hemisphere over Svalbard, Norway, of -2.4%/year in February. Given that the photochemical conditions (insolation, temperatures) are so different in the two hemispheres (although PSCs are seen in both), it is not clear that the Northern Hemisphere depletions could be attributed to the same chemical mechanism.

In short, until the mechanism(s) responsible for the O_3 reductions are understood, the global implications will remain unclear.

5.2.5 Observations in Antarctica, Spring 1987

By the time this lecture is given a number of observation campaigns will be underway in Antarctica. Ground based (column) measurements of O_3, NO_2, OClO, BrO, aerosol and temperature will again be made from McMurdo Base (78°S). The more major component will be flights by 2 NASA aircraft into and through the vortex. The aircraft (an ER-2 and a DC-8) will fly in the stratosphere at altitudes between 11km and 19km during the second half of August and September. Summaries of the aircraft payloads are shown in Table 1. The range of measurements should allow both chemical and dynamical theories of the ozone depletion to be tested.

ER-2 payload (summary), altitude 18-20km, up to 73°S

Measurement	Type	Remarks
O_3	in situ	self evident
ClO, BrO	"	direct chemistry
nitrogen oxides	"	"
H_2O	"	PSCs, origins
Knollenberg/CN counter	"	particle sizes - PSCs
N_2O, whole air	"	origins of air

DC-8 payload (summary), altitude 11km, cross pole flights

Measurement	Type	Remarks
O_3	in situ, lidar(12-20km)	self evident
aerosol	lidar(12-20km)	PSCs
H_2O	in situ	PSCs, origins
N_2O whole air	"	origins
composition (various)	column	chemistry

Table 1: Summary of Aircraft Payload for the Antarctic Ozone Expedition

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WMO Global Ozone Research and Monitoring Project Report no. 16 (1986).

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G.C. Reinsel and many others, Journal of Geophysical Research, 92, pp 2201- 2209, (1987).

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M.P. McCormick and C.R. Trepte, Journal of Geophysical Research, 92, pp 4297-4306 (1987).

Production of Cl_2O_2 by the self reaction of the ClO radical.
L.T. and M.J. Molina, Journal of Chemical Physics, 91 pp433-436 (1987).

Circulation changes and chemistry: implications for the destruction of ozone in Antarctica.
J. Austin, R.L. Jones, T.N. Palmer and A.F.Tuck, submitted, Nature (1987).

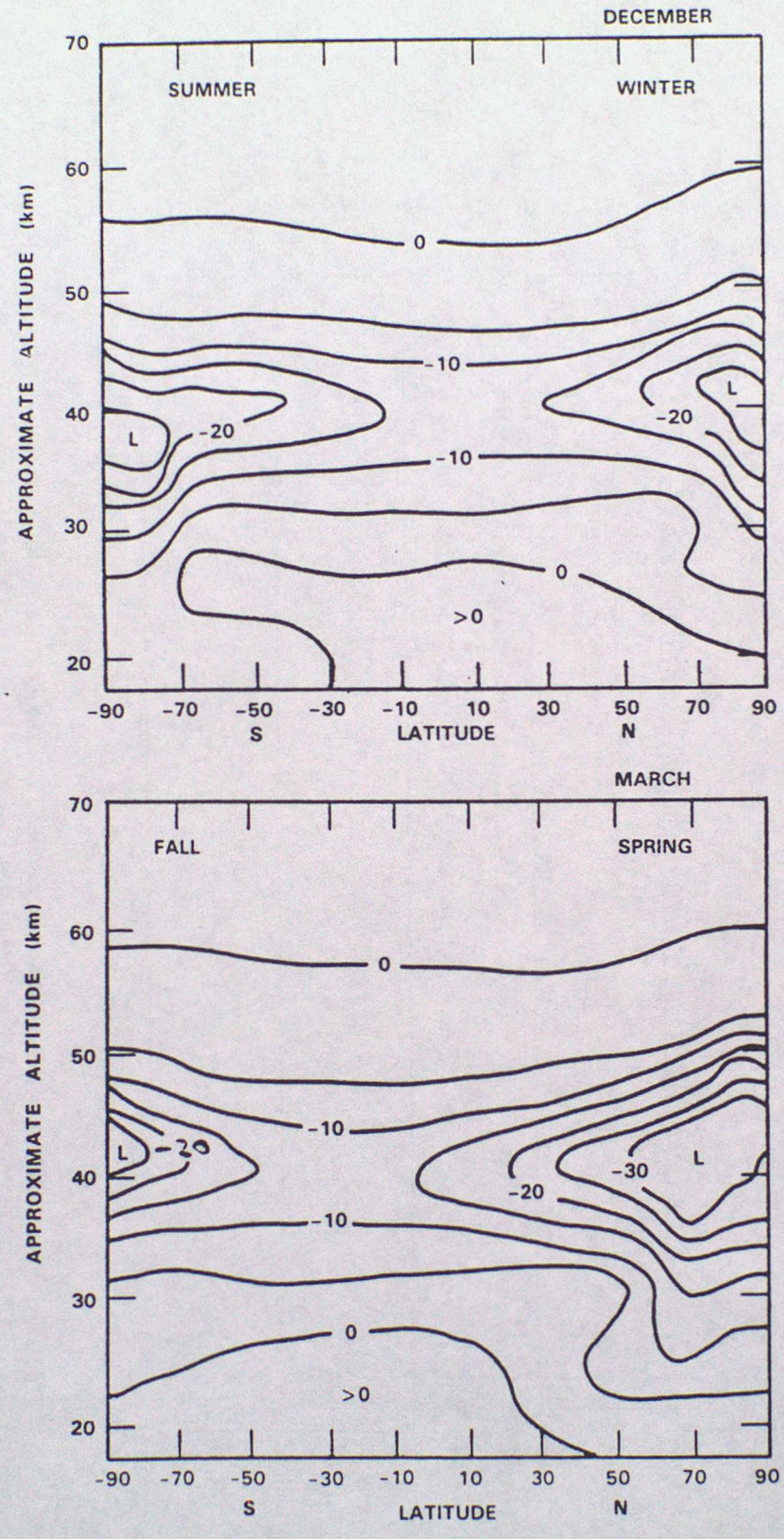

Figure 1 Percentage changes in zonal mean ozone between 1965 and 1985 calculated using a 2 d (latitude-height) numerical model. Only chlorine was perturbed (1.3ppbv to 2.7ppbv).

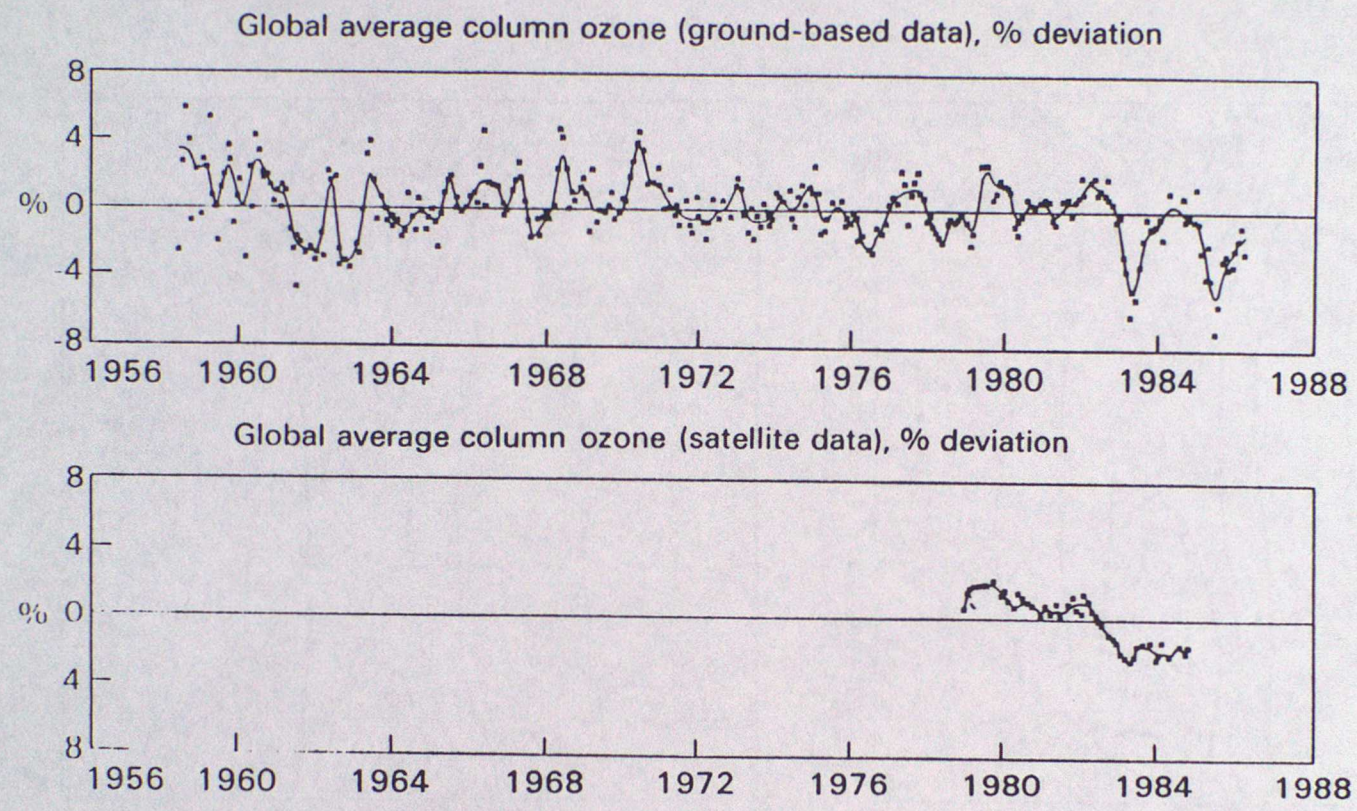

Figure 2 Monthly mean values of globally averaged column ozone obtained from the Dobson network (top panel) and from the SBUV instrument on Nimbus 7 (bottom panel). Seasonal fluctuations have been removed in both cases.

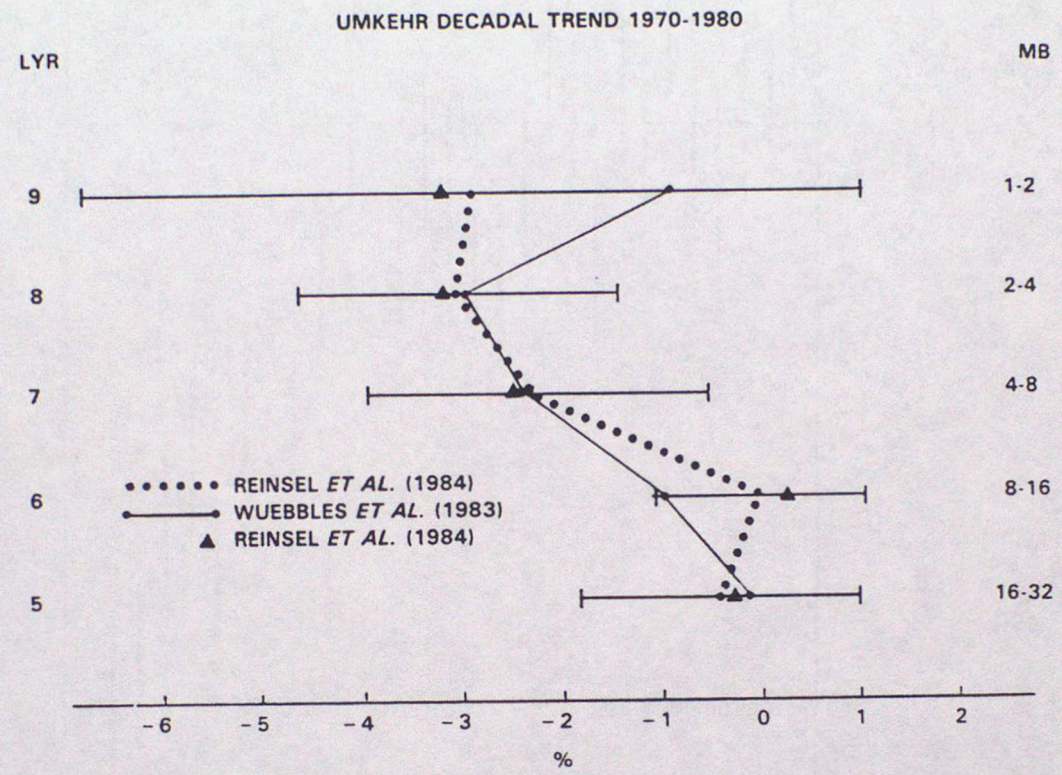

Figure 3 Umkehr decadal trend 1970-1980 at different atmospheric levels (% per decade).

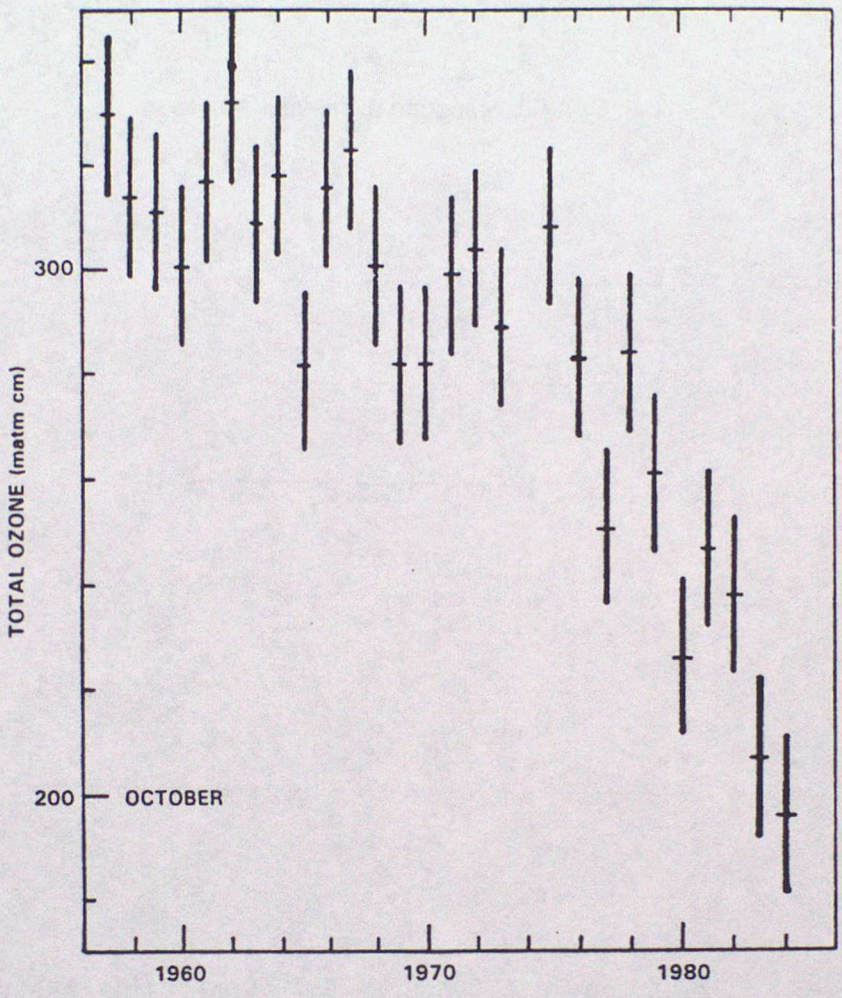

Figure 4 Monthly means of column ozone at Halley Bay for Octobers of the years 1957-1984.

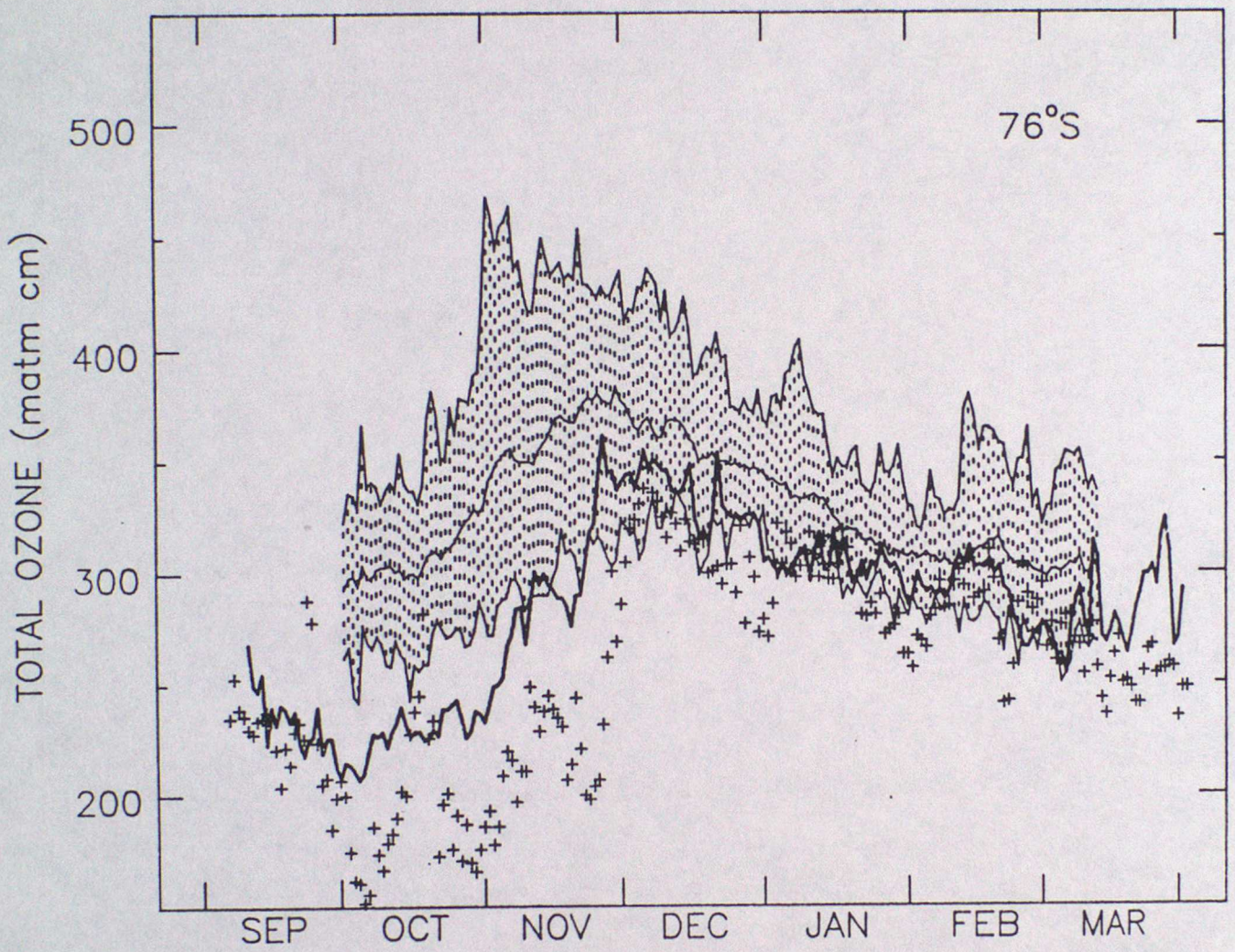

Figure 5 Mean and extreme daily values of column ozone over Halley Bay, 1957-73 (hatched), with mean daily values for 1980-1984 (solid line) and daily values for 1985 (crosses).

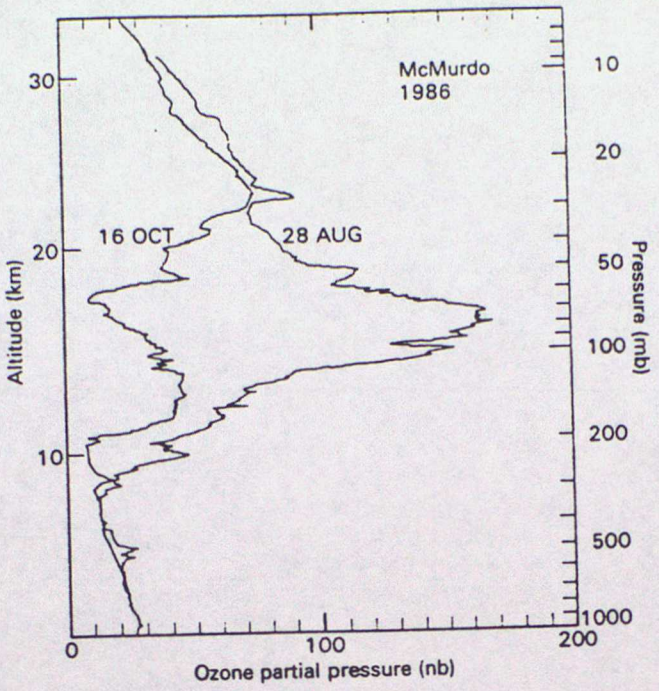

Figure 6 Ozone profiles from balloon soundings over McMurdo Base (78S) taken on the 28th August and 16th October 1986.

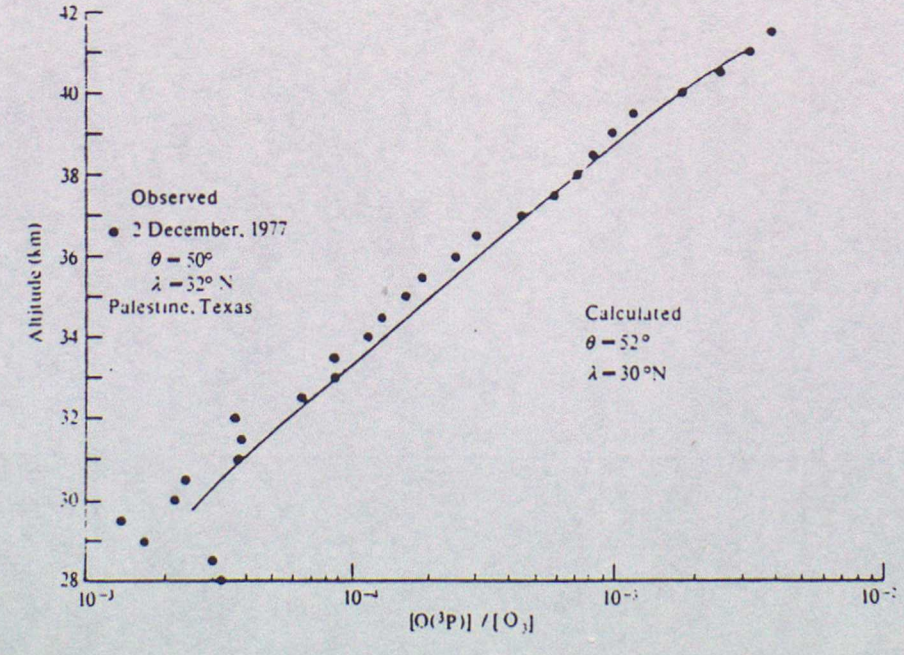

Figure 7 Calculated and observed ratios of $[O]/[O_3]$.

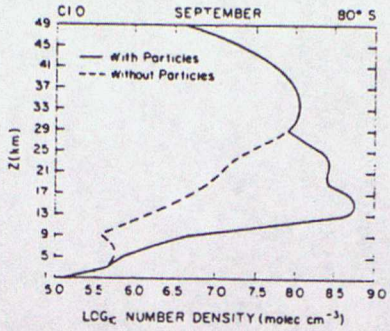

Figure 8 Number density of ClO within the Antarctic vortex in September as a function of altitude, with and without the heterogeneous reaction h1 (see text).

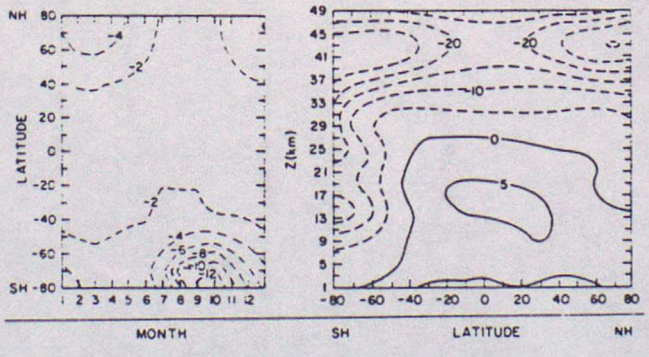

Figure 9 Calculated ozone changes (%) due to increases in stratospheric chlorine (1 to 2.7ppbv) and bromine (15 to 30pptv). The left panel shows the column change as a function of latitude and season The right panel shows altitude-latitude changes for September.

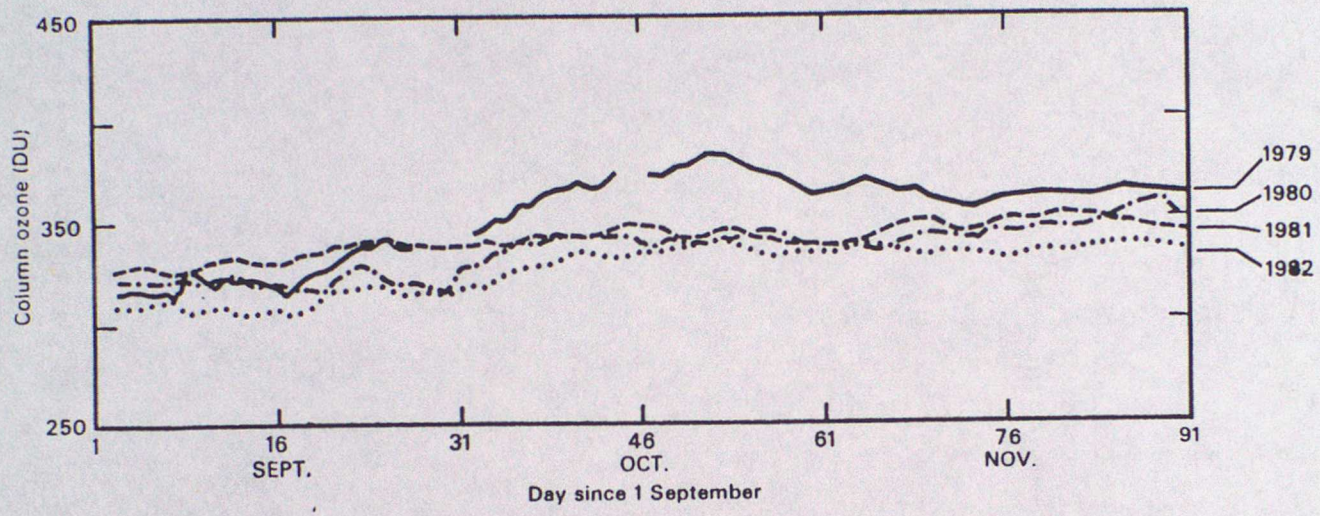

Figure 10 Daily area weighted integral of column ozone from 44S to the pole, from 1st Sept. to the 30th Nov., 1979 to 1982.

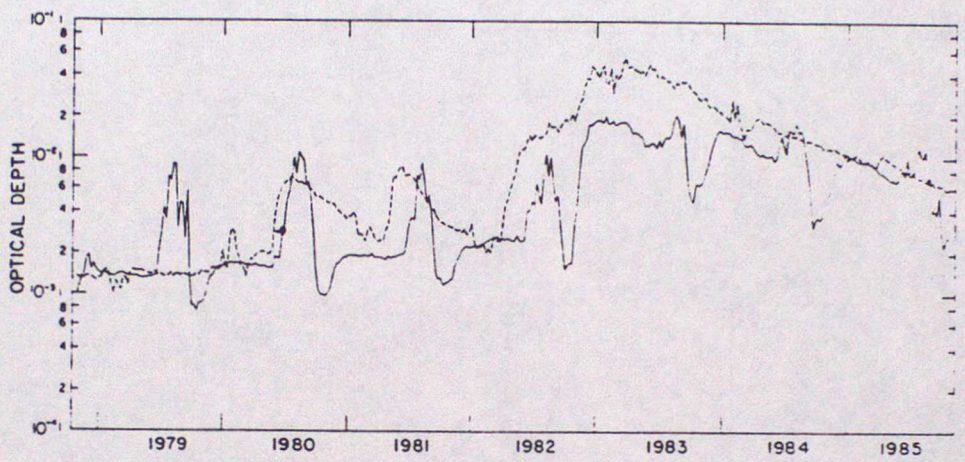

Figure 11 Weekly averaged SAM II stratospheric aerosol optical depth at 1μm from October 1978 to October 1985. The optical depth is calculated from the 200mb surface upward.

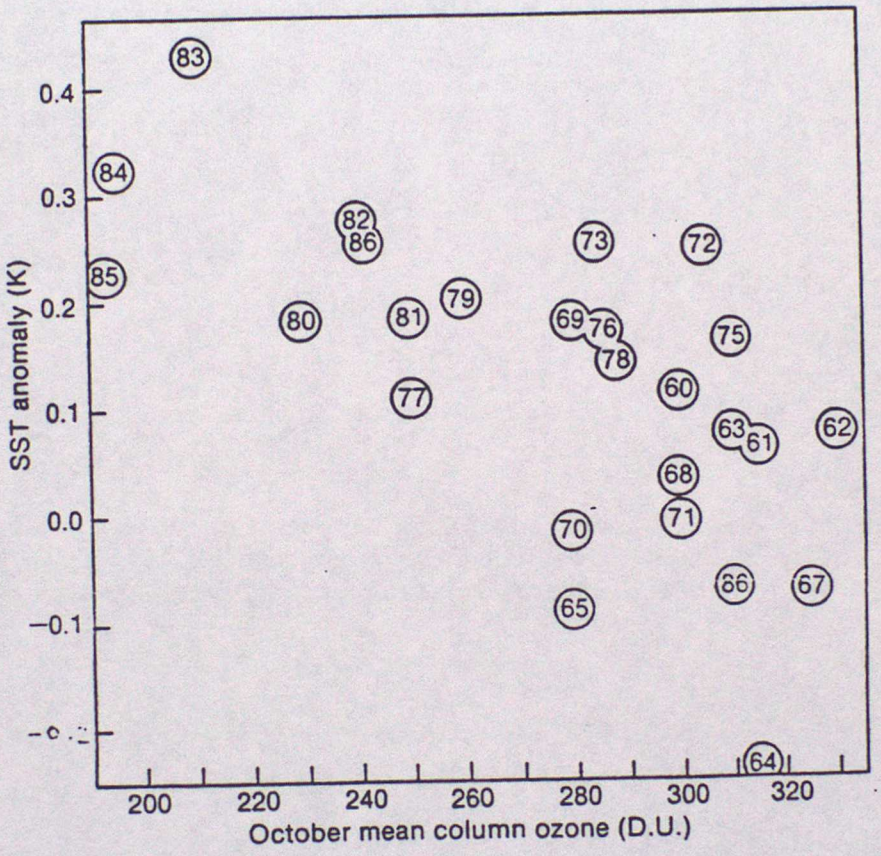

Figure 12 Southern Hemisphere Jul-Aug-Sep sea surface temperature anomaly relative to 1951-80 plotted against Halley Bay October mean column ozone.

6. An Overview of Tropospheric Chemistry.

6.1 Introduction.

There is a growing concensus that the levels of ozone in the troposphere are increasing (Derwent,1987). Unfortunately our ancestors did not expect us to make such dramatic perturbations to the atmosphere and so did not establish any monitoring network for the species we now know to be important . If we wish to deduce levels of these gases prior to recent times when there has been ever increasing monitoring activity, we usually have to be very clever and deduce historic records from various kind of proxy data which has been stored in the geologic, sedement or ice records. As yet no proxy for ozone has been devised, and we are left with only a few dubious measurements made by a variety of techniques. Many of these techniques relied on moist paper impregnated with chemicals which have a colour response to ozone. Recently many of these techniques have been studied by Kley,who has gone back and tried to calibrate many of these them against modern ozone monitoring equipment. He concluded that many of these methods are much better at measuring humidity than they are at measuring ozone.

However there is one data set from the Montsouris Observatory near Paris which he believes can be reliably calibrated. These data set are compared against the best modern data available from Arkona, Germany (Fig 1). At best they hint that there might

have been a trend but one should be very careful at interpreting this data, since the two curves are from different sites by different techniques at different altitudes. In addition to the longterm increases suggested by Fig 1 there is also an increase in what are termed pollution episodes.These are periods usually during the summer months when polluted boundary layer air is exposed to extended periods of sunlight,this results in elevated levels of ozone which may persist for many days.Fig 2 shows data collected earlier this year by some of the stations of the Department of the Environment groundbased ozone monitoring network.As you can see starting from the 23rd of April 87 high levels of ozone were observed, for several days. Ozone has a number of effects which make increased levels in the troposphere undesirable:

- o Ozone is a greenhouse gas.
- o Ozone cases health problems.
- o Ozone damages crops.
- o Ozone is a secondary pollutant and any increase in ozone would be followed by increases in PAN and other secondary pollutants which also have adverse effects.

We will spend the rest of this lecture discussing how ozone relates to the chemistry of the troposphere,and

how it may be produced or destroyed.

6.2 Tropospheric Photochemistry.

The levels of incoming solar radiation are much lower in the troposphere than they are in the stratosphere since much of the shortwave radiation has been absorbed by the ozone layer. From Fig 3 we see that the tropospheric radiation levels at short wavelenths are much less than at 15km. However there is still sufficient energy at appropriate wavelengths to initiate an elaborate range of chemical reactions.

Most chemical paths involve at a very early stage reaction with the hydroxyl radical. Thus any discussion of tropospheric chemistry must include a description of this radical. We will start by exploring how the hydroxyl radical (usually denoted by symbol -OH) can be produced photochemically. While the amount of ozone in the free troposphere is much lower than in the stratosphere (typically a few tens of parts per billion by volume (ppbv) , Fig 4) and the intensity of the radiation capable of initiating photolysis of ozone molecules is much reduced there is still sufficient 'leakage' to initiate a complex set of chemical reactions (Seinfeld,1986,p113). These will usually start with,

$$O_3 + h\nu \longrightarrow O_2 + O\cdot(^3P) \quad 310nm < \lambda < 400nm \qquad (1a)$$

$$O_3 + h\nu \longrightarrow O_2 + O\cdot(^1D) \quad \lambda < 310nm \qquad (1b)$$

the ultimate fate of the $O(^3P)$ atom is to recombine with molecular oxygen and reform the ozone molecule.

6.3 The Hydroxyl Radical.

However, $O(^1D)$ has potentially a much more interesting fate. Though most of the $O(^1D)$ produced is quenched to ground state $O(^3P)$, a small but significant number will encounter water molecules and will react to give hydroxyl radicals.

$$O\cdot(^1D) + H_2O \longrightarrow 2OH\cdot \qquad (2)$$

This is the primary reaction and is involved in much of the photochemistry which goes on the troposphere.

Now for what is thought to be one of the most important chemical species in the atmosphere it is useful to try and get a feel for what the concentration are likely to be. From reaction (2) we can express the rate of production of OH as:

$$d/dt[OH] = J_{O^1D}k_2[O_3][H_2O]$$

The major losses of OH are via the oxidation of carbon monoxide and methane.

$$\cdot OH + CO \longrightarrow CO_2 + \cdot H \qquad (3)$$

$$\cdot OH + CH_4 \longrightarrow H_2O + \cdot CH_3 \qquad (4)$$

Assuming that the loss and production of OH are in

balance (steady state) then we can estimate the concentration of OH from a knowledge of the incoming solar radiation at the appropriate frequencies and the concentrations of ozone, water vapour, carbon monoxide and methane.

$$[OH] = \frac{\alpha J_{O_3} k_3 [O_3][H_2O]}{k_4[CO] + k_5[CH_4]}$$

where α the branching ratio for reaction (1b)

is $\alpha = 0.0028$

$k_4 = 2.80 \times 10^{-13}$ $cm^3/mol.sec$

$k_5 = 2.40 \times 10^{-12} exp(-1710/T)$ $cm^3/mol.sec$

If we assume typical values for temperature, mixing ratios and photolysis rate. e.g.

$[O_3]$ = 40 ppbv

$[CO]$ = 277 ppbv

$[CH_4]$ = 1650 ppbv

$J_{O_3} = 8.03 \times 10^{-6}$ sec^{-1}

then

$n_{OH} = 3 \times 10^{+5}$ mol/cm^3

therefore at the surface since

$n_{OH} = [OH].n_{M}$

$[OH] = 1.23 \times 10^{-5}$ ppbv

That is a very small number of radicals.

Considerable ingenuity has gone in to developing techniques suitable for measuring OH at these very low concentrations (Perner & Hubler,1982), but there is as yet no technique which produces results which are not open to considerable doubt.

Now that I have impressed you with how insignificant the OH concentration actually is I will go on and demonstrate just how important it is!

Reactions (4) & (5) both produce new radical species which are very reactive and react rapidly with molecular oxygen to produce peroxide radicals.

$$H + O_2 \longrightarrow HO_2$$

$$CH_3 + O_2 \longrightarrow CH_3O_2$$

One of the sinks for peroxide radicals is self reaction i.e.

$$HO_2\cdot + HO_2\cdot \longrightarrow O_2 + H_2O_2$$

to produce hydrogen peroxide and an oxygen molecule. If however there is a small amount of NO available then these peroxide radicals can react with the NO to produce nitrogen dioxide and regenerate the hydroxyl and methoxyl radicals once again thus:

$$HO_2\cdot + NO \longrightarrow NO_2 + OH\cdot$$

and,

$$CH_3O_2\cdot + NO \longrightarrow NO_2 + CH_3O\cdot$$

which can be followed by,

$$CH_3O\cdot + O_2 \longrightarrow HCHO + HO_2\cdot$$

so that after three steps the second of these more complex radicals can regenerate primary OH radicals.

6.4 Photostationary state.

In order to get a better feel for how the chemical systems , which we are going to be interested in, behave it is instructive to backtrack and start with a slightly different mix of chemicals. Consider a system which contains only three stable trace gases O_3, NO & NO_2 in an excess of O_2 and N_2, what would be the chemistry which would go on in such a system? For our purposes we need only consider the three reactions:

$$O_3 + NO \longrightarrow O_2 + NO_2 \quad (1)$$

$$NO_2 + h\nu \longrightarrow NO + O \quad (2)$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (3)$$

Reaction (2) the NO_2 photolysis is an important reaction Fig 5 & 6 show the absorbtion of NO_2 in the visible. Notice from Fig 7 how much greater the absorbtion rate is for NO_2 compared to O_3. If this system is irradiated at visible wavelengths and only these reactions are important then within a few minutes

these three species will establish an equilibrium which only depends on the initial mixing rations of the three compounds and the intensity of the radiation. This equilibrium is usually refered to as the photostationary state, and the expression which links the concentrations of the three species:

$$[O_3] = \frac{J_{NO_2}[NO_2]}{k_3[NO]}$$

is refered to as the photostationary state relation. This relation is still approximately obeyed, in more complex situations, provided there are no cycles which equilibrate faster than the $NO-NO_2$ cycle.In order to constrain the concentrations fully we must consider the stoiciometery of the $NO-O_3$ reaction and conservation of nitrogen. When we take account of these factors we can deduce that the steady state O_3 concentration is given by the expression:

$$[O_3] = 1/2([NO]_o-[O_3]_o+J_{NO_2}/k_2) + 1/2(([NO]_o-[O_3]_o+J_{NO_2}/k_2)^2 + 4J_{NO_2}/k_2([NO_2]_o+[O_3]_o))^{1/2}$$

typically J_{NO_2}/k_2 might have a value of 10 ppbv. If the initial O_3 concentration is much greater than the concentrations of NO and NO_2, then the steady state concentrations will be very close to the initial O_3 concentration. This expression is valid only for the specific case of the O_3-NO_2-NO system described above. The only source of ozone in this reaction scheme is O atoms generated by photolysis of NO_2, i.e. any NO_2

which is formed will be quickly photolysed and generate on ozone molecule.Also the only source of NO_2 is the reaction of NO with O_3 so there is an upper limit on the number of ozone molecules in the system ($[NO_2]+[O_3]$). Later we will see that NO_2 can be generated by reactions which do not involve O_3 destruction which means the number of O_3 molecules can increase above this photostationary state limit.

6.5 Water Vapour.

If we wished to introduce a slightly more realistic set of equations then we could consider the same mixture of trace gases and also watervapour. Previously the only route available to the oxygen atoms produced by O_3 photolysis was recombination with O_2 to reform O_3, this is a closed loop which neither creates or destroys ozone and therefore it was not necessary to include it in the present analysis. However, we must consider the branch of the O_3 photolysis which generates excited oxygen atoms ($O(^1D)$) since these can react with water and generate OH radicals. Thus we must consider:

$$O_3 + h\nu \longrightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \longrightarrow 2\text{-}OH$$

$$OH + NO_2 \longrightarrow HNO_3$$

The nett effect of these extra reactions is to reduce the number of NO_2 molecules, which will reduce the

steady state ozone concentration, i.e. the ozone photolysis is acting as a nett sink of ozone. In practice the NO_2 photolysis will be much more rapid than the reaction with OH and so this will only represent a very small sink for O_3, it is also a sink which depends on the amount of NO_2 available and which consumes NO_2 in the process. The nitric acid produced in these reactions can either be photolysed back to NO_2 and OH or it can be rained out. Since it is water soluble, nitric acid formation is regarded as a termination reaction in the troposphere. There are a number of reactions which involve OH reaction with O_3 but these do not produce any additional nett changes in the O_3 concentrations.

6.6 Carbon Monoxide.

The next increase in complexity that we could consider is achieved by introducing carbon containing species. The simplest carbon compound we can consider is carbon monoxide (CO). The principle reactions which we need to consider is:

$$CO + \cdot OH \longrightarrow CO_2 + H\cdot$$

$$H\cdot + O_2 \longrightarrow HO\cdot_2$$

the second step in this sequence is extremely fast and we can usually represent it as one step, i.e.

$$CO + \cdot OH + O_2 \longrightarrow CO_2 + HO\cdot_2 .$$

The peroxide radical formed in this reaction can become involved in a number of reactions, principly.

$$HO_2 + O_3 \longrightarrow OH + 2O_2$$

$$HO_2 + NO_2 \longrightarrow OH + NO_2$$

These reactions are very significant both regenerate the OH radical which the cycles started from and in the process oxidized one CO molecule to CO_2. Thus provided there is more CO available these reaction can be repeated without any further O_3 photolysis. The nett effect of these two cycles is however quite different in one important respect;the first has destroyed an ozone molecule while the second has generated an ozone molecule, since it converted an NO molecule to NO_2 without involving ozone. Because in both cycles the OH radicals which initiated the reaction are regenerated, these cycles are described as catalytic.

How can we establish which of these two cycles will be is the most important? There are two threshholds involved. Initially if there is no CO available all the OH will eventually react with NO_2 and be lost to the system. Once there is sufficient CO present to effectively compete with the NO_2 then the CO reaction will begin to be important,with a consequent increase in HO_2 production. In order to determine whether there will be any significant HO_2 production we must consider the ratio of the reaction rates of OH with CO and NO_2, we can define a chain length (L_c)

which will indicate how many times an OH radical can cycle through the HO_2 formation reactions, before it is terminated by reaction with NO_2.

$$L_c = k_{CO}[CO]/k_{NO2}[NO_2]$$

since we require the chain length to be greater than unity for this process to be significant we can establish a critical CO-NO_2 ratio:

$$[CO]/[NO_2] = L_c.k_{CO}/k_{NO2}$$

$$k_{CO} = 2.4x10^{-13}$$

$$k_{NO2} = 2.4x10^{-11}$$

$$L_c = 1.0$$

Thus if there is any significant HO_2 generation:

$$[CO]/[NO_2] > 100$$

i.e. the CO mixing ratio must exceed the NO_2 mixing ratio by at least a factor of 100. Since in the clean background troposphere NO_2 may be measured in fractions of a part per billion while CO is measured in hundreds of parts per billion, i.e. their ratio is about 10^3, CO reaction with OH will be a significant pathway. The next threshhold which we need to consider is the competition between O_3 and NO to react with HO_2. While it is not a chain length (but the ratio of two chain lengths) the ratio of the appropriate reaction rates indicates whether there is nett ozone production or

destruction.

$$R = k_{NO}/k_{O3} \cdot [NO]/[O_3]$$

$$k_{NO} = 8.3\times10^{-12}$$

$$k_{O3} = 2.0\times10^{-15}$$

$$R = 4.15\times10^{3}[NO]/[O_3]$$

If R > 1, NO should win over O_3 for reaction with HO_2 and there should be a nett gain in ozone, while if R < 1, then O_3 wins over NO and there should be a nett lose of ozone. Typical clean air values of $[O_3]$=20 ppbv and [NO]=0.001 ppbv would suggest that the clean troposphere is a nett sink of ozone.However, if background levels of NO were to increase from 1 pptv to 5 pptv, then much of the free troposphere could become a nett source of ozone. Thus we see that in the free troposphere the critical quantity is the O_3-NO ratio which dictates what the ozone regime is, since in practice there is always a excess of CO.

6.7 Methane oxidation

So far we have only been dealing with the very simplest carbon compound CO, the next step in increasing complexity is to consider, methane. By considering methane we introduce some more reactions which make life more complicated but we can still extract some simple features which are very important. As with CO the first step in the methane chemistry is reaction with OH, thus:

$$CH_4 + OH + O_2 \rightarrow CH_3O_2 + H_2O$$

This is the methane oxidation process which is a major source of water vapour in the stratosphere. The methylperoxyl radical generated reacts with NO in the same way as HO_2 to generate NO_2 (and then O_3) and produces a methoxyl radical

$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

Once the second HO_2 radical has reacted with an NO molecule it will have generated two ozone molecules for each cycle. But that not all, we have also formed a formaldehyde molecule (HCHO). Formaldehyde has a complex chemistry. Initially it can react with OH or it can be photolysed to give either radicals or stable molecules. Depending on which way the reaction goes it can produces either one or two ozone molecules and an extra OH radical for each ozone produced. Thus methane oxidation can produce several new ozone molecules and either one or two new OH radicals, so that for every methane oxidized we would expect to create more ozone and accelerate the oxidation process.

Methane oxidation is however a much slower process than carbon monoxide oxidation because the rate of hydroxyl attach for methane is

$$k_{CH_4} = 7.7 \times 10^{-15}$$

which is about two orders of magnitude slower than CO oxidation rate. However important features of much of the hydrocarbon chemistry has been illustrated namely that during the methane oxidation process there has effectively been a branching step since formaldehyde is much more easily photolysed in the troposphere than ozone, i.e. that step introduces more free radicals into the system and so accelerates the hydrocarbon oxidation. This has been a rather simplified version of methane chemistry but it does illustrate a number of important points on a relatively simple molecule. However the reactions of OH with higher hydrocarbons is generally faster than methane and so when these hydrocarbons are present they can play an important role.

6.8 Polluted vs Clean.

In the clean unpolluted (free troposphere) troposphere the chemistry will be dominated by the availability of NO_x (NO or NO_2) which would appear to be the critical factor in controlling ozone production/loss. In the polluted boundary layer the situation is somewhat different. We have shown that for the CO-OH reaction to be effective over the NO_2-OH reaction the CO mixing ratio has to exceed the NO_2 mixing ratio by a factor of at least 100. The figure of 100 being based on the relative reactivities of CO and NO_2 to OH. When considering a mix of reactive

hydrocarbons the situation is not quite so simple or so readily analysed. One has to to resort to a complex photochemical model which includes explicitly the detailed hydrocarbon reactivities. The nett effect is to increase overall hydrocarbon reactivity to the point where it is almost comparable to NO_x reactivity. What this means is that OH is as likely to react with NO_x and form nitric acid as it is to react with a hydrocarbon and release HO_x. Which process actually controls depends critically on the relative concentrations of NO_x and total reactive hydrocarbon content.

Up till now we have been distinguishing between a polluted atmosphere and a clean atmosphere and have assumed that there is a staightforward definition of what a 'clean' atmosphere consists of (or doesn't consist of?). However it is worth going deeper into this point. The use of the word polluted is really quite imprecise. A reasonable definition of pollution would be:

- When levels of one or more anthropogenic gases are such that (adverse) effects are experienced.

The trouble with this definition is that it could be applied throughout the troposphere. In the troposphere the levels of CO are such that there is an anthropogenic component in all of the northern hemisphere and probably much of the southern hemisphere

as well, Fig 8, (see WMO,1985,vol I). One should therefore distinguish between a modern 'clean' atmosphere and a preindustrial 'clean' atmosphere. Since most NO_x emissions are anthropogenic, we might speculate that the clean preindustrial atmosphere contained relatively few trace gases compared to clean atmosphere today. There would still be some CH_4 about from natural emissions and therefore some CO from CH_4 oxidation and some ozone from the stratosphere. It is likely that NO concentrations were much lower than we experience today since they would only derive from natural emission from the soil and some produced by lightning which we consider unimportant relative to anthropogenic sources. This would imply that the troposphere was an ozone sink through catalytic destruction of O_3 and the formatiom of nitric acid (these sinks were probably not as important as destruction at the ground).

By contrast a modern background atmosphere is a much richer soup of chemicals. There is now much higher levels of both nitrogen oxides and hydrocarbons and the status of the background troposphere as a nett source or sink of ozone is now much more in the balance.

Then there is the polluted atmosphere which can be described as containing gases of recent anthropogenic origin usually at levels of 100's of ppbv. It will contain NO & NO_2, from car exhaust, powerstations and agriculture (mainly NO), CO and hydrocarbons, again from combustion sources and will

generally be a much more reactive soup of chemicals.

6.9 Stable Secondary Pollutants.

There are however classes of molecules which make even these definitions problematic. These molecules are usually secondary pollutant (i.e.they are not emitted but are formed in the atmosphere). They can under certain cicumstances be longlived. One such product of the so called 'smog' reactions, is PeroxyAcetyl Nitrate or PAN. This is a complex molecule whose main sink is thermal decomposition. This decomposition has a very strong temperature dependence so that the PAN lifetime is short near the surface but at lower temperatures becomes much longer lived. PAN decomposes via the following reaction:

$$CH_3COO_2NO_2 \xrightarrow{k_1} CH_3COO_2\cdot + NO_2$$

(PAN)

$$CH_3COO_2NO_2 \xleftarrow{k_2} CH_3COO_2\cdot + NO_2$$

(PAN)

$$k_1 = 7.94\times10^{+14}\exp(-12540/T)\ s^{-1}$$

$$k_1/k_2 = K = [PAN]/([CH_3COO_2\cdot].[NO_2])$$

NO can compete with NO_2 to react with the peroxyacetyl radicals via the abstraction reaction,

$$CH_3COO_2\cdot + NO \xrightarrow{k_3} CH_3COO\cdot + NO_2$$

followed very quickly by,

$$CH_3COO\cdot \longrightarrow CH_3\cdot + CO_2$$

we can estimate the lifetime of the PAN molecule now by assuming that the peroxyacetyl radical is in steady state. From that assumption we can show that,

$$d/dt(\ln[PAN]) = -k_1(1+1/(1+k_3[NO]/k_2[NO_2]))$$

and the e-folding time for PAN destruction is given by

$$t_e = 1/k_1(1+(k_2/k_3)([NO_2]/[NO]))$$

where $k_2/k_3 = 0.54$

As we can see from the foregoing analysis the most important feature in controlling PAN destruction is temperature. So if we reduce the ambient temperature to near zero we expect PAN to be long lived. Therefore any PAN which reaches the lower temperature of the free troposphere could remain there for some time, PAN is further assisted in transfer to the free troposphere by being relatively insoluble in water which means that it is not easily rained out.

Thus PAN, species in the same family as PAN, and other organic nitrates can be longlived, they are nevertheless suceptable to chemical reactions or decomposition so that even the clean background troposphere could have rather complex chemistry

(Leighton,1961).

PAN and molecules like it can be regarded as temporary NO_2 reservoirs, Fig 7 shows how much less sensitive to radiation PAN is compared with NO_2. This means that NO_2 can be taken out of a reactive system and stored in an unreactive form until there is a temperature increase. Once out of the boundary layer an airmass which containes PAN could be advected intact for many thousands of miles, if that air then found itself in a warmer boundary layer elevated levels of NO_x could be experienced along with the corresponding consequences for ozone production, many miles downwind of the initial source regions.

6.10 Control Strategies.

If we accept that there has been an increase in surface O_3 and we wish to take steps to halt or reverse this trend then we have to consider control strategies. There are two elements of the ozone production process which we can in principle modify, the levels of NO_x and the levels of hydrocarbons. One of the main sources of both of these is car exhausts. If we plotted ozone production as a function of NO_x and hydrocarbons mixing ratio we would produce a diagram known generically as 'the isopleth diagram' Fig 9. The actual values in such a diagram depend on what mix of hydrocarbons is selected, the light intensity and the model formulation. However most diagrams do contain the same basic feature, a characteristic ridge which identifies

the maximum ozone production for a given duration of irradiation.

The shape of this diagram can be rationalized in terms of the processes which we have already discussed. Below the ridge axis the hydrocarbons are effectively in excess and ozone production is limited by NO_x. Above the axis The NO_x is beginning to become comparable to the hydrocarbons in its reaction with OH and so hydrocarbons are now limiting ozone production. The control strategy that one would then adopt would be very different depending on where in the diagram the atmosphere one wished to control actually fell. Above the axis reductions in NO_x would <u>increase</u> ozone production, but reductions in hydrocarbons would lead to reductions in ozone. Below the axis reductions in NO_x would reduce ozone production, while reductions in hydrocarbons would have little effect. This may all seem very simple and straight forward and just what a policy maker needs to allow him (or her!) to make a well informed and reasoned decision. However there are a number of pitfalls in such a simple approach. Recall that this diagram is based on a fixed duration of exposure. The oxidation of hydrocarbons can only have just begun. If we look more closely at one of the model runs which went into constructing Fig 9 we would find results similar to those in Fig 10. We see most of the features that we might expect, ozone increasing, hydrocarbons decreasing and NO_x decreasing as NO_2 reacts with OH to form nitric acid. The important point to note about this diagram is that only a small

amount of the hydrocarbons available has been consumed. As the oxidation process continues the horizontal parts of the isopleths move down the diagram as more of the ozone is produced. If there is sufficient NO_x available all of the hydrocarbons must eventually be oxidised to CO_2 and at that time the diagram should look more like a series of vertical lines i.e. independent of NO_x concentration. Fig 9 would assist someone in identifying the local effect of emission controls, since it would indicate what the ozone production was near the source, but would not be much use when discussing the overall global effect of emissions, and emission reductions.

6.11 Conclusions.

o NO and NO_2 react to O_3 levels so that all three are always in balance on time scales of more than a few minutes. It is this very rapid response to changes in any one of the three species which leads to urban reductions in O_3 due to excess NO emitted in motor vehical exhausts.

o In the free troposphere the ozone production / destruction depends critically on the levels of NO relative to O_3.

o The chemistry involved in the oxidation of non-methane hydrocarbons is complex and leads to the production of many ozone molecules and several

radicals.

o The chemical reactions which take place in the troposphere can lead to long lived species which can provide long range transport for chemically active species and so lead to photochemical ozone production in the remote atmosphere.

o The effect of reduced emissions of NO_x may have either good or bad effect on the local ozone climate. Reductions in hydrocarbons may not produce reductions in either local ozone levels or to reductions in global ozone production.

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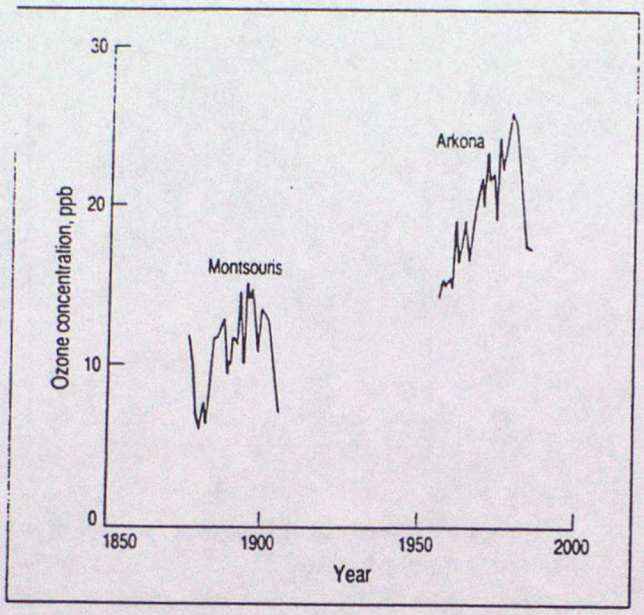
Fig1



Near-surface ozone concentrations measured at Montsouris, France 1876 – 1905 and Arkona, German Democratic Republic 1956 – 1984.

Fig 2

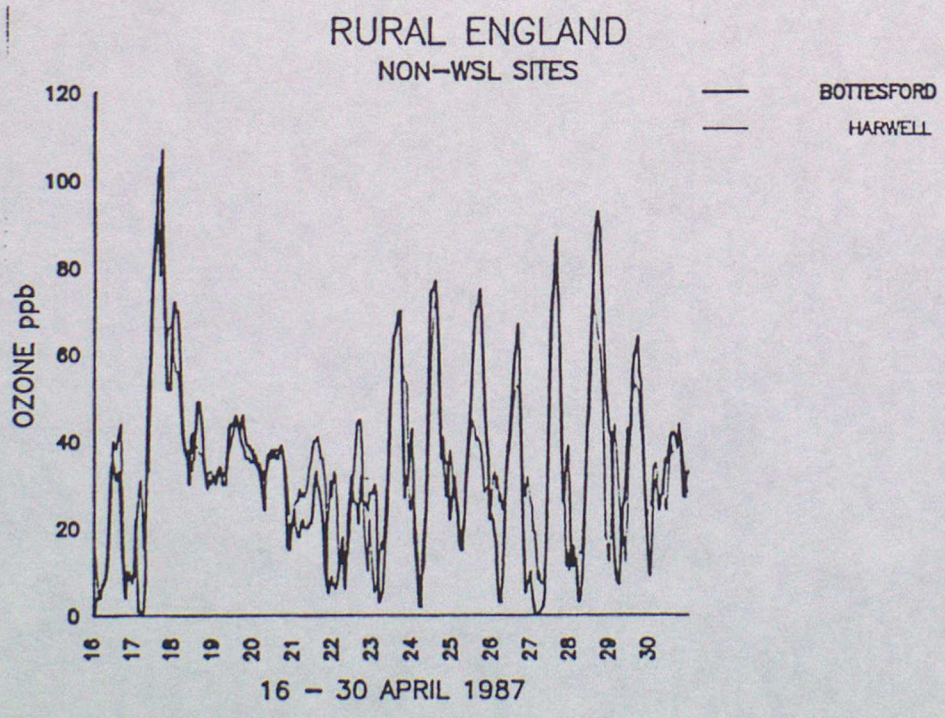
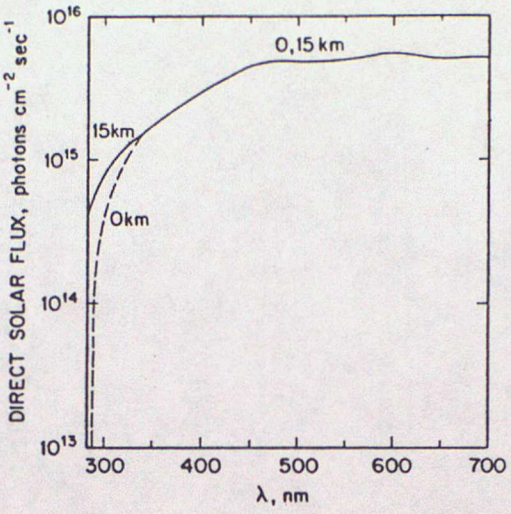
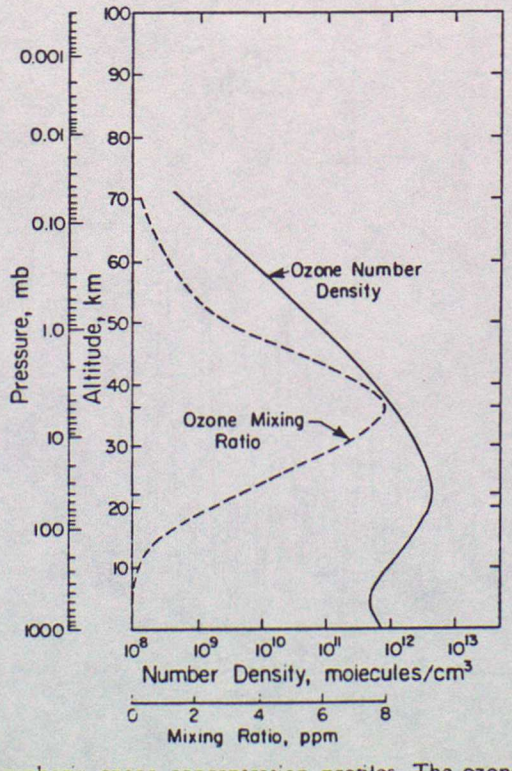


Fig 3



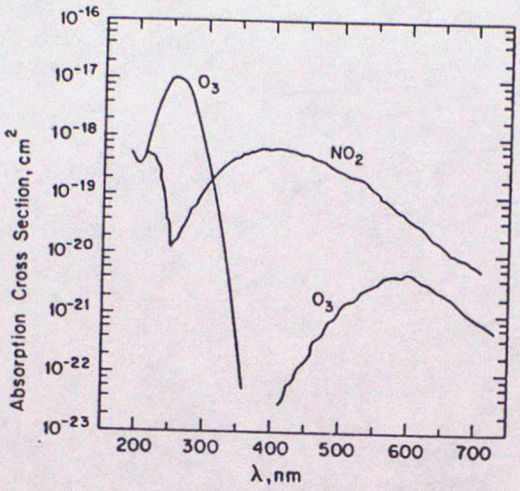
Direct solar flux at 0 and 15 km as a function of wavelength (National Center for Atmospheric Research, 1982).

Fig 4



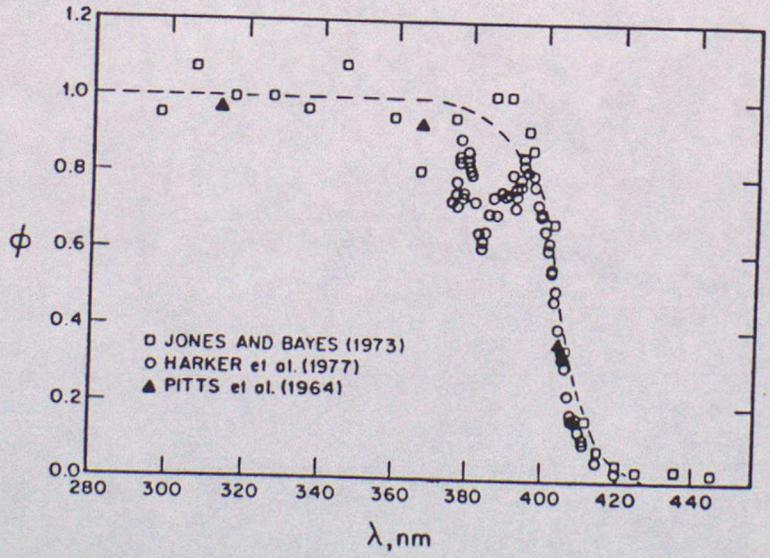
Atmospheric ozone concentration profiles. The ozone concentration is shown in terms of both number density and mixing ratio.

Fig 5



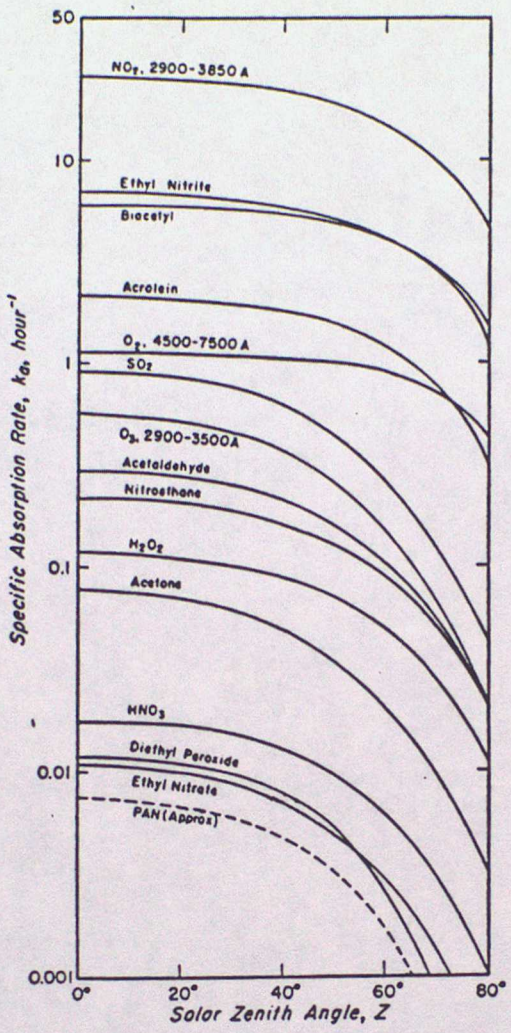
Absorption cross sections for O_3 and NO_2 in the uv and visible regions of the spectrum (Luther and Gelinas, 1976).

Fig 6



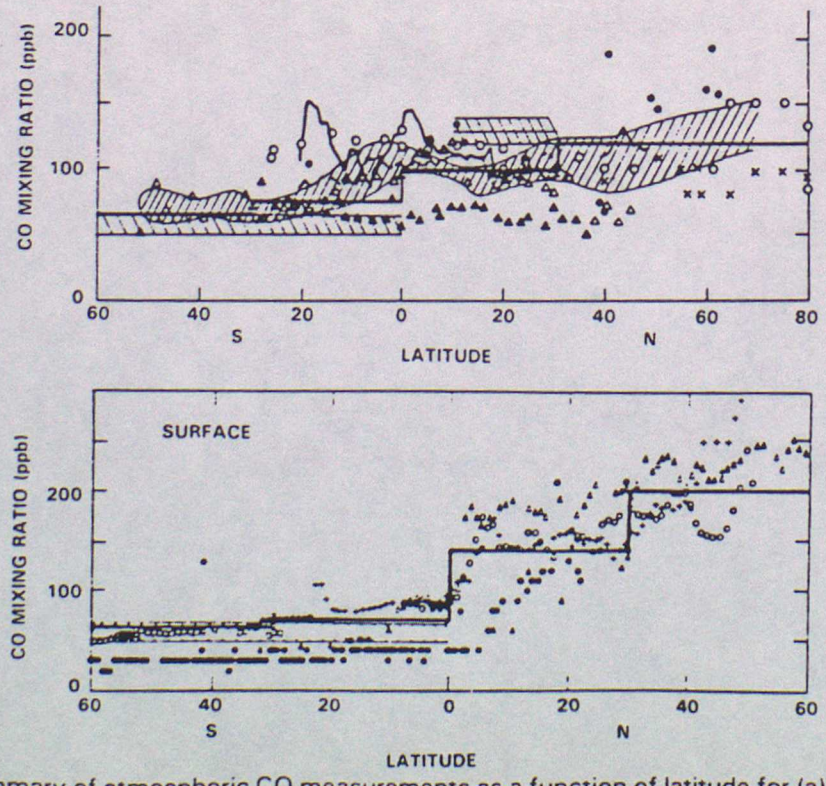
Experimental quantum yield data for the production of atomic oxygen (O) from the photolysis of NO_2 as a function of wavelength. The dashed line represents the quantum yields suggested by Demerjian et al. (1980).

Fig 7



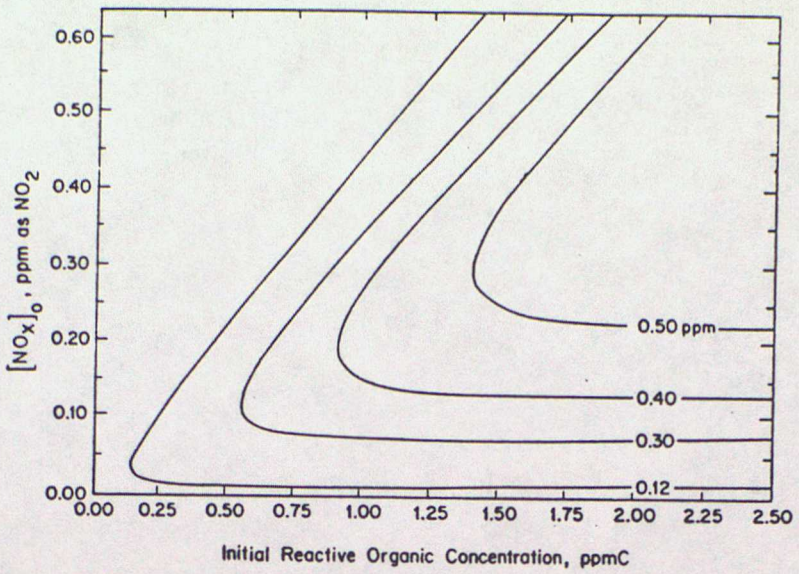
Summary of specific absorption rates.

Fig 8



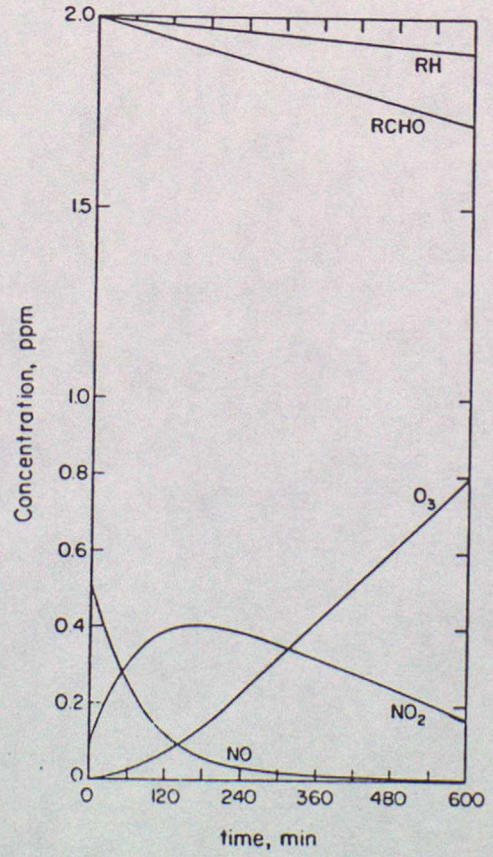
Summary of atmospheric CO measurements as a function of latitude for (a) mid-troposphere and (b) surface for the period 1967-78 (from Logan *et al.*, 1981). The heavy lines show average values for latitude zones 0, 30° (N,S) and 30, 90° (N,S).

Fig 9



Ozone isopleth plot. The maximum O_3 concentration achieved during a fixed time of irradiation of a mixture whose initial concentrations are $[NO_x]_0 = [NO]_0 + [NO_2]_0$ and $[Organic]_0$, where the latter is measured in parts-per-million of carbon (ppmC). Although the general features of this plot are duplicated in virtually all photochemical smog systems, the actual location of the O_3 isopleths depends on the specific conditions of the irradiation, such as the particular components of the organic mixture, the light intensity, and so forth.

Fig 10



Concentrations predicted by a generalized reaction mechanism for photochemical smog.

7. The Sulphur cycle.

7.1 Introduction.

The main interest in the sulphur cycle has been driven by the 'acid' rain problem. As such the understanding of the anthropogenic inputs into the atmosphere are much better understood than any other aspect of the cycle, including the contributions from from agricultural runoff and industrial sources (Ivanov&Freney,1983). The main reservoirs are the same as for the other species which we have been discussing. A block representation of the sulphur cycle is shown in Fig 1

7.2 The lithosphere.

This the largest sulphur reservoir contains 4×10^{20} g atom S mostly as sulphate or sulphide, but also some elemental sulphur. The sulphur is transfered to the lithosphere via sedimentation processes at a rate of 4×10^{12} g atom S per yr. The nett transfers out of the lithosphere are via weathering associated with river runoff which accounts for 4.25×10^{12} g atom S per yr to the hydrosphere and fossil fuel combustion which releases 2×10^{12} g atom per yr into the atmosphere.

7.3 The pedosphere.

Some authors suggest that the pedospheric reservoir is as large as the lithospheric reservoir, but that may arise from including some lithospheric contributions twice (Delwiche,1984). The main sinks are river runoff and biological decay which adds a further 2×10^{12} g atom S to the atmosphere. This value is required to balance the pedospheric budget. The main sources are weathering of sulphur rich sediments, the application of sulphur fertilizer and wet and dry deposition which collectively contribute 3×10^{12} g atom S per yr to the pedosphere.

7.4 The hydrosphere.

This reservoir containes 4×10^{19} g atom S, mostly as sulphate, but also some reduced organic sulphur. The source terms for the hydrosphere include the runoff from rivers, the atmospheric deposition of sulphates at a rate of 2×10^{12} g atom S per yr, and absorption of SO_2 by sea water at a rate of 0.5×10^{12} g atom S per yr. The sulphur content of the oceans is increasing at a rate of 1.25×10^{12} g atom S per yr,this implies that there is an imbalance between the sources and sinks.For many years it was been thought that there had to be an extra sulphur flux from the oceans to the land in order to balance the hydrospheric reservoir even after this trend has been

taken into account. Many authors suggested hydrogen sulphide (SH_2) as a suitable candidate molecule but it has only recently been shown that the missing sulphur flux was due to dimethyl sulphide (DMS).The flux of DMS from the oceans to the land is 1.5×10^{12} g atom S per yr. (Nguyen et al,1978).

7.5 The atmosphere.

This is the smallest reservoir with only 0.05×10^{12} g atom S. With sinks totalling 5×10^{12} g atom S per yr this gives a mean residence time in the atmosphere of only 4 days. The atmospheric reservoir is made up of a number of gases which have a variety of physical and chemical lifetimes. Sulphur dioxide which is oxidized into sulphate has only a very short residence time with respect to precipitation. DMS and hydrogen sulphide are both rapidly oxidized to SO_2. The remaining atmospheric sulphur exists as OCS. OCS is a gas with both biogenic and anthropogenic sources would appear to have an atmospheric lifetime of ~2 yrs. Because OCS is unreactive in the troposphere and not water soluble, it can survive in the atmosphere long enough to reach the stratosphere. There OCS is oxidized in a number of steps until it eventually forms sulphuric acid. This is thought to be one of the sources (along with direct volcanic emissions) of the stratospheric sulphate aerosol layer.

The two main oxidation states of sulphur are S(IV) and S(VI).S(IV) includes SO_2, sulphides and

sulphurous acid,while S(VI) includes SO_3,sulphates and sulphuric acid.In the troposphere sulphur which is deposited on the land has at some time existed as SO_2 whether that sulphur was origionally of manmade or natural origin. If one recalls O-level chemistry you will remember that the solvation of SO_2 in water leads to the formation of sulphurous acid which is only weakly dissociated (in the present context dissociation is the process of forming ionic species) . It is a well established empirical fact that the sulphur component of acid precipitation is almost invariably sulphuric acid (Barrett et al,1987), a completely dissociated acid. Since the only direct source of S(VI) is sea spray (which is only of secondary importance), it should be clear that for this to be the case SO_2 (S(IV)) has to be oxidized to sulphate (S(VI)) in the atmosphere . There are a number of possible routes whereby this oxidation can take place. The most likely gas phase process involves reaction of SO_2 with the hydroxyl radical, this reaction is not very rapid, but will contribute eventually to the dry deposition of sulphate [see lecture 6 for more on the hydroxyl radical]. However to explain the rapid oxidation of SO_2 we must resort to the aqueous phase chemistry .

7.6 Aqueous Phase Sulphur Chemistry.

Like CO_2, SO_2 is water soluble, and behaves in a similar fashion. Differences arise because of the larger equilibrium constants of the sulphur species

(Seinfeld,1986,p201). Generally SO_2 is much more soluble than CO_2 and the hydrated forms will dissociate more readily than the hydrated forms of CO_2 .

$$SO_2 + H_2O \rightarrow SO_2.H_2O \qquad K_{HS}$$

$$SO_2.H_2O \rightarrow H^+ + HSO_3 \qquad K_{S1}$$

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \qquad K_{S2}$$

The concentration of hydrated SO_2 is given by:

$$[SO_2.H_2O] = K_{HS}.p_{SO_2}$$

Comparing SO_2 and CO_2:

Eqilibrium Constants	SO_2	CO_2
K_H	1.24	3.4×10^{-2}
K_1	1.3×10^{-2}	4.3×10^{-7}
K_2	6.0×10^{-8}	4.7×10^{-11}

If we are dealing with initially pure water , we can establish what the pH should be if it is in equilibrium with a specified mixing ratio of either gas (pH is defined to be $-\log_{10}[H^+]$). For normal atmospheric conditions the hydrogen ion concentration can be approximated by:

$$[H^+] = (K_w + K_H K_{S1}.p_{gas})^{1/2}$$

If we assume a typical CO_2 mixing ratio of 330ppmv then

$$pH_{CO_2} = 5.66$$

This value is usually taken as the pH of pure rain water and so preciptation acidity is judged against this standard. If we assume 1 ppbv of SO_2 in eqilibrium over a flat surface then we have:

$pH_{SO_2} = 5.4$

Thus we can see that SO_2 is much more acidic than CO_2.

If we change the pH of the solution then the above result would no longer apply. However we can still calculate the effect of pH on these equilibria. As with CO_2 the partitioning of the three possible states of SO_2 in water depends on the pH of the solution. From Fig 2 we see that at progressivly low pH (i.e. more acidic, more H^+ ions) the partitioning shift first from SO_3^{2-} to HSO_3^- and then at the lowest pH to the hydrated SO_2. We can understand these result by considering the S(IV) equilibrium reactions. The solubility products are related the the equilibrium concentrations by the expression.

$$K_{HS} = [SO_2.H_2O]/p_{SO_2}$$

$$K_{S1} = \frac{[HSO_3^-].[H^+]}{[SO_2.H_2O]}$$

$$K_{S2} = \frac{[SO_3^{2-}].[H^+]}{[HSO_3^-]}$$

As the solution is made more acidic (by some independent means), the H^+ concentrations will increase. However the solubility products for each reaction remain fixed, in order to satify these relations, the HSO_3^- and SO_3^{2-} concentrations must decrease. Thus at low pH all the S(IV) resides as $SO_2.H_2O$. At intermediate pHs the solubility of SO_2 is partially successful in overcoming the ionic effect and so we get some HSO_3^- in solution. Finally when we get weakly acidic or alkaline conditions we have more

SO_3^{2-}. The dependence on pH means that in neutral or alkaline conditions a fixed volume of water can accomodate more SO_2 than in acidic conditions, i.e. as the pH decreases the SO_2 is pushed out of solution. Fig 3 shows the ratio of the total dissolved sulphur to the hydrated SO_2. This neatly illustrates the point that at low pH there is no dissociated SO_2. Thus if we were interested in a reaction with one particular form of SO_2 then we would expect the reaction rate to be pH dependent.

7.7 Sulphur Oxidation.

It is known that there is no significant reaction between dissolved oxygen and dissolved sulphur dioxide.To produce sulphate we must look further to see where the oxidatizing agent may come from. In fact there a several metal ions which promote the oxidation of SO_2 but we will consider the example of O_3 oxidation of SO_2. The reaction of ozone with sulphur dioxide to produce sulphate has been studied extensively and the rate equation for the reaction is thought to be:

$$-\frac{d[S(IV)]}{dt} = (k_0[SO_2.H_2O]+k_1[HSO_3^-]+k_2[SO_3^{2-}])[O_3]$$

where,

$k_0 = 2.4\times10^4$ $(Msec)^{-1}$

$k_1 = 3.7\times10^5$ $(Msec)^{-1}$

$k_2 = 1.5\times10^9$ $(Msec)^{-1}$

Thus SO_3^{2-} is much more reactive than either HSO_3^- or $SO_2.H_2O$ by many orders of magnitude. Since the

concentration of each species is dependent on pH, there will be a strong preference to react with SO_3^{2-} initially ,for typical atmospheric conditions. This oxidation will consume one ozone molecule and one SO_3^{2-} ion for each SO_4^{2-} produced, but will not by itself change the pH. However because a SO_3^{2-} has been removed the equilibrium between the various species in the SO_2 reactions will favour the uptake of more SO_2 which will eventually be oxidized. Each time another SO_2 molecule goes into solution the pH will drop. Each time the pH drops SO_3^{2-} becomes less soluble (see Fig 2) and so the rate of oxidation of S(IV) to S(VI) will be reduced. Fig 4 shows how the rate of oxidation depends on pH for ozone and a number of other oxidizing agents. If there is excess SO_2 in the atmosphere then as more S(IV) is converted to S(VI) the pH will gradually shift to lower pH. As this happens the rate of oxidation will decrease, S(IV) is in equilibrium when most of the sulphur is contained in the less reactive species. Eventually the S(IV) partitioning reaches a steady state and no further SO_2 can dissolve and the droplet has become much reduced in oxidizing efficiency.

Almost all S(IV) oxidising methods exibit similar pH dependence and are not as efficient as O_3 oxidation. The one notable exception to this is hydrogen peroxide (H_2O_2), this is a secondary pollutant formed during photochemical reactions in the atmosphere. H_2O_2 initiated oxidation does not exibit strong pH dependence and is more efficient than O_3 at

most pHs. However its effectivness in oxidizing S(IV) is limited by its abundance, since H_2O_2 is present at concentrations well below plume SO_2 concentrations and one peroxide is consumed for each sulphur oxidised, all the peroxide is very quickly consumed and ozone is then the most efficient oxidiser. Ozone is not very soluble in water so that in practice the S(IV) oxidation rate is usually limited by the rate of transfer of ozone to the droplet, until that is the pH dependence of the reaction rate becomes dominant and effectively shuts down any further oxidation.

The rate at which S(IV) is oxidised is very dependent on the pH of the solution which in turn depends on the initial partial pressure of SO_2. We would expect on purely chemical arguments that sulphur oxidation will be less efficient at high atmospheric SO_2 concentrations than at low SO_2 concentrations. It is not that less sulphur is oxidised in the high concentration case but, the sulphur which is oxidised represents a smaller fraction of the total sulphur burden. The sulphur that we are particularly interested in when considering these reaction is emitted as exhaust gases in power station plumes, as a result of burning sulphur rich fuels.

7.8 Long Range Transport.

An important aspect of the non-linear dependence of oxidation rate on SO_2 concentrations is that a high concentration plume will have an SO_2

lifetime with respect to wet-deposition which is longer than the lifetime in low concentration plumes. Therefore we would expect high concentration plumes to have a longer range than low concentration plumes. Also if for some reason the levels of ozone or some other oxidant were depleted then again we might expect that this would increase the atmospheric residence time, because the wet oxidation process was not effective. Thus because of the intrinsic non-linearity we expect that the range of sulphur pollutants will be greater than would be predicted from a deposition model which has a linear parameterisation of oxidation and deposition. We still expect the total deposition to be the same, but it will just be spread over a larger area.

Downwind of the United Kingdom we might expect to see a source plume with ~12 ppb of SO_2. While downwind of a group of powerstations a plume may have SO_2 levels nearer 60 ppb (Clark,1987). If we assume 50 ppbv of ozone (quite a high background value), and bare in mind that ozone is several orders of magnitude less soluble in water than SO_2, we might expect that both these plumes would experience non-linear effects due to the unavailability of ozone as well as SO_2 concentration effects.

The non-linearity in SO_2 oxidation and deposition has been used to argue that because this can not be properly treated in a linear model that the effects of emission controls on deposition can not be predicted by a linear model, and that for a 50%

reduction in emissions the reduction in deposition may be much less at a given receptor, and we should therefore model the processes very carefully before we decide what control strategies to employ.

7.9 Deposition Modelling.

There have of course been various attempts to do what has been suggested using trajectory models which include gas and aqueous phase reactions. These have been used to explore the emissions problem and control stategies. We will discuss a much less sophisticated model which tries to model the basic effects of the non-linearity in a statistical sense. Results from this model suggests that in the long term averages the deposition response is much more linear than one might expect, by considering single precipitation events.

This model, developed by Smith (1986), is a very simple attempt at predicting the consequences of the non-linearity on emission controls. The model consists of an air parcel, which extends from the surface to the top of a boundary layer of constant height,and is advected away from an SO_2 source by a constant wind. Sulphur can be lost from the parcel by dry or wet deposition, the rate of dry deposition is a constant factor while the wet depostion depends on the SO_2 concentration in a non-linear fashion. Wet deposition events are modelled by assuming a constant rainfall rate, and assuming the transition from wet to

dry period can be modelled by a Markov process. The model results can be regarded as significant if the important quantity when estimating effects is ths average deposition, the model tells us nothing about the likely effects, ona single rainfall event of, emission controls . Smiths model selected a function of SO_2 concentration, which has the expected functional dependence on SO_2,but which is otherwise quite arbitrary, he argues that any non-linearity should behave in this way and that though the quantitative results would change depending on the choice of function that the qualitative results should be robust to such modifications (in practice a more physically realistic functional form devised by (Clark,1987) has a similar form). The SO_2 oxidation rate employed by Smith is given by:

$$\frac{d[SO_2]}{dt} = - \frac{[SO_2]}{1-\epsilon[SO_2]}$$

The range of ϵ is from $\epsilon = 0$ the linear case to $\epsilon = 1$ the maximum non-linearity possible.It has been argued that the effective randomness of the rainfall process would smear out much of the non-linearity associated with one rainfall event and therefore the system is in the long term more linear than might at first be expected. Fig 5 shows the percentage reductions experienced at receptors at various distances from a source. This shows that as we reduce the quantity of sulphur emitted the benefits are greater than 50% for receptors more than a few hundred km away from the source.However, near the source region though the

deposition has been reduced it has not been reduced by as much as 50% because now more efficient oxidation of S(IV) means that relatively more SO_2 gets oxidized and depositied nearer the source.

This work starts from the premise that it is the average deposition which is the important factor, and shows that given that assumption the result of reduced emissions is very likly to be proportional reductions in contributions to depositions from that source. Of course it will have no effect on the emissions from other sources or from the unattibuted (natural?) background source of sulphate. It has been pointed out that it may not be the mean acid deposition which is causing environmental damage, but the statistically extreme events which may deposit the equivalent of several months of mean S(VI) deposition in a single rainfall event.

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Fig 1

Sulfur Cycle

Reservoirs : 10^{12} g atom S
Fluxes : 10^{12} g atom S per yr

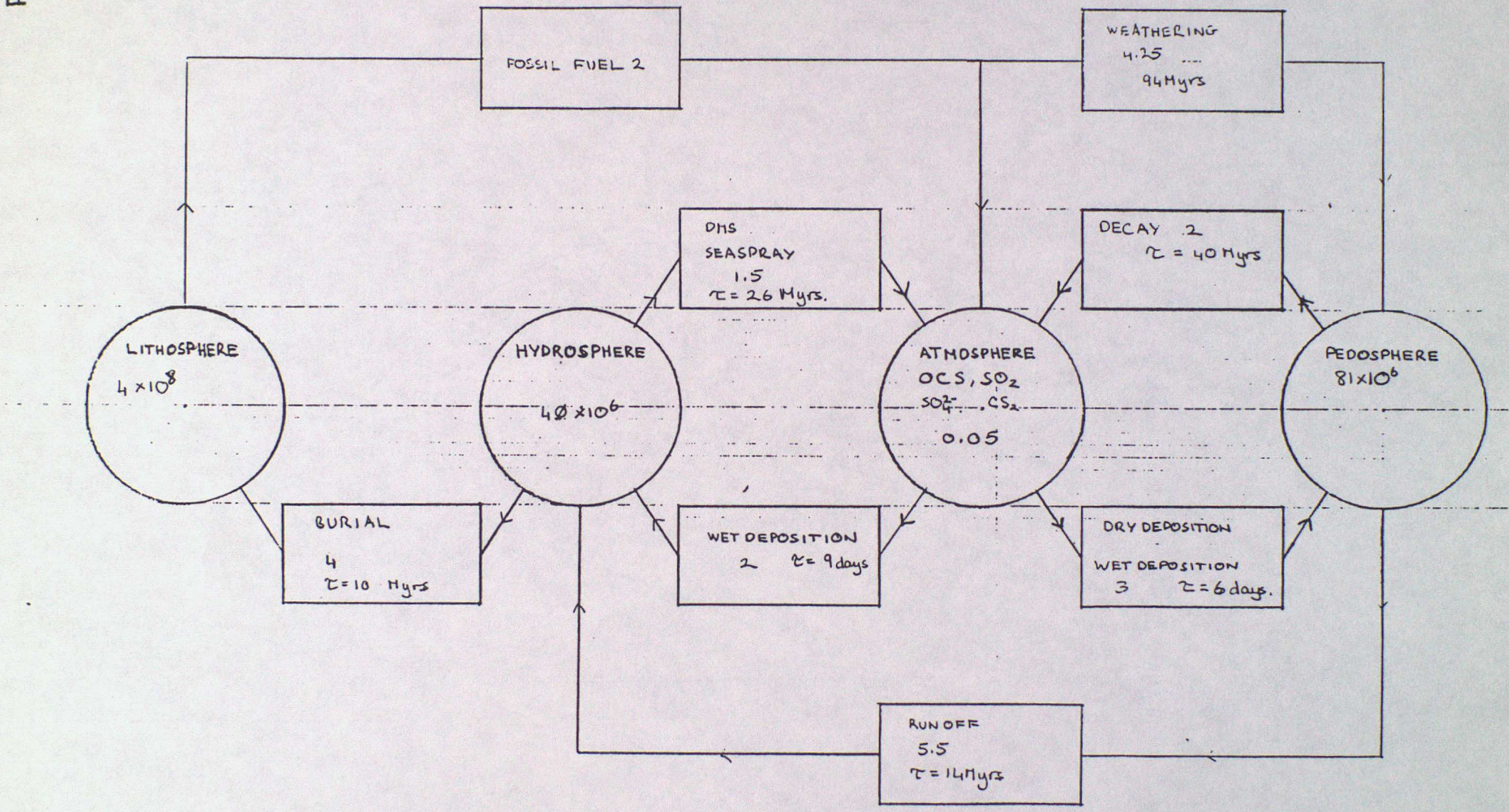
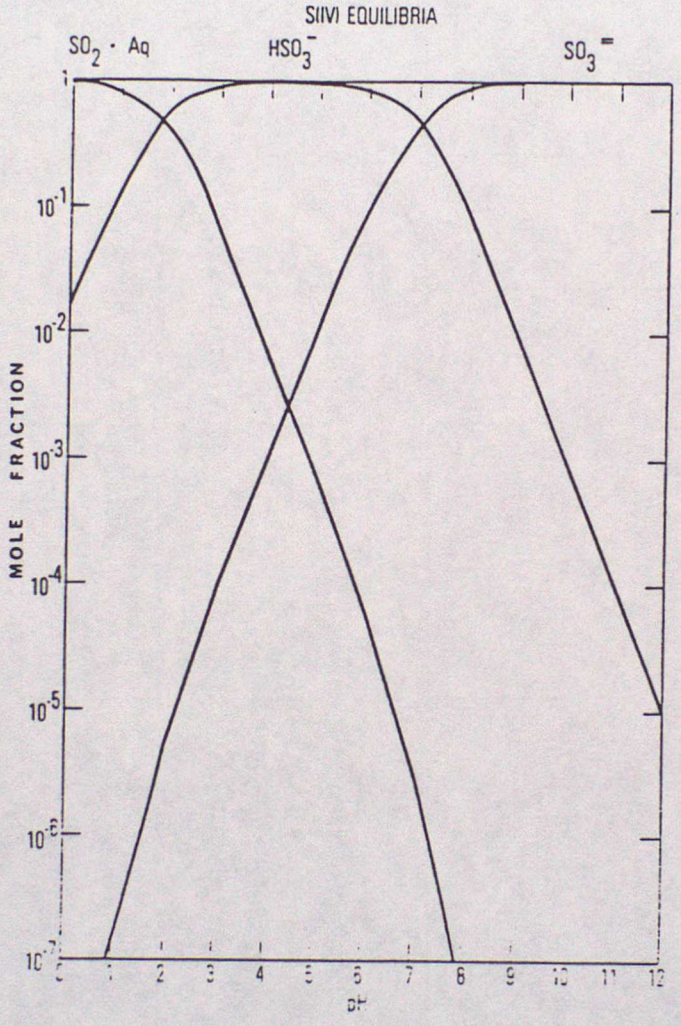
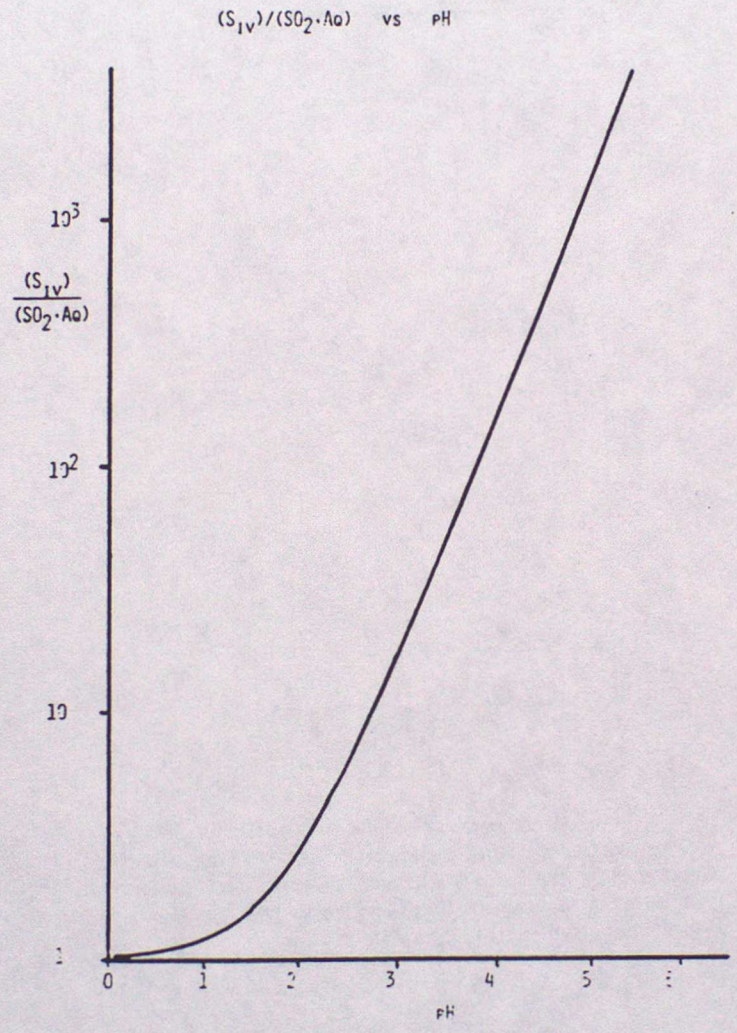


Fig. 2.



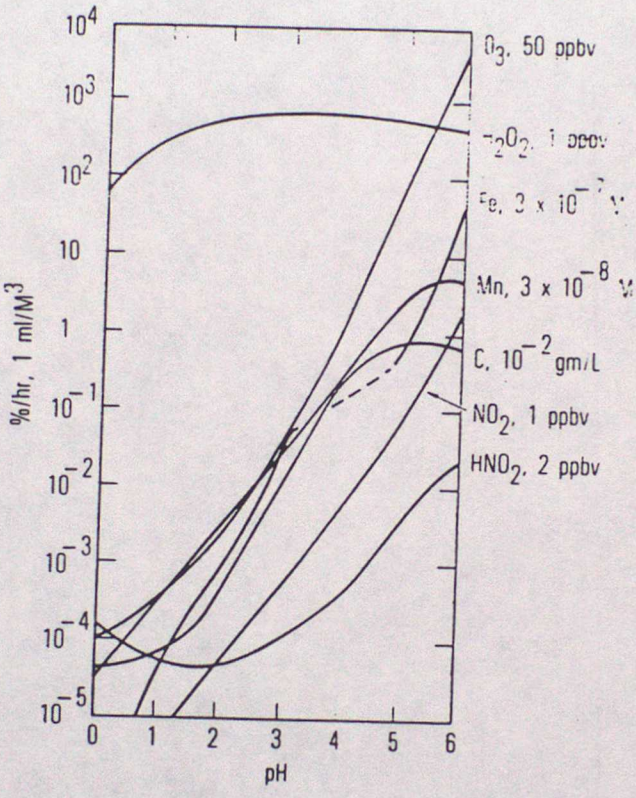
Relative concentrations of the three sulfur(IV) species as a function of pH. Reproduced with permission from *Atmospheric Environment*.

Fig 3.



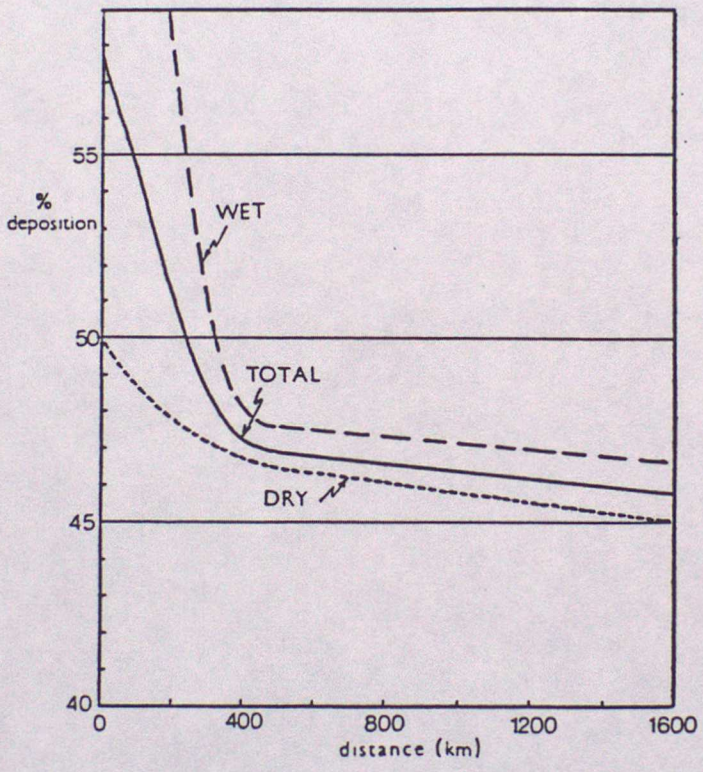
Ratio of total sulfur(IV) to the hydrated oxide.

Fig 4



Percent per hour oxidation of total sulfur(IV) in a cloud containing 5 ppb (volume) of SO_2 and 1 mL of liquid water m^{-3} for the various reactants and processes described in the text. It is assumed that there are no rate limitations due to mass transport; temperature = 25 C.

Fig 5


55
50
45
40
% deposition
WET
TOTAL
DRY
0
400
800
1200
1600
distance (km)

Lecture 8: Models of Atmosphere Chemistry I

by Dr.J.Austin

8.1. Introduction

In the previous lectures the full complexity of atmospheric chemistry has been illustrated. To understand quantitatively how chemical processes behave requires a detailed mathematical model of the system involving interactions with radiation and dynamics. However, limitations in computing power mean that not all aspects of this highly interactive system can be represented in the same model and a wide variety of techniques exist which concentrate on just some aspects of the problem.

Broadly speaking , models can be classified as 1,2,or 3 dimensional and there is an additional category which includes trajectory modelling and box modelling. Trajectory modelling consists of the computation of air parcel trajectories and the integration of a detailed chemical model along them. The technique is well suited to the stratosphere for those periods when sufficient data exist. Box models may be considered as special cases of trajectory models but with the wind fields set to zero. Results from these models are described in the next lecture. Three dimensional models attempt to represent the full

complexity of the dynamics and radiation but have so far been little used for photochemical studies. Some attempts have been made to incorporate simple chemical schemes and these are reviewed in the next lecture. Two dimensional models contain simplified (zonally averaged) dynamics so that almost the full photochemistry can be represented. Their major weakness lies in the rather unrealistic parameterisation of the effect of Rossby wave dynamics. Despite this there have been considerable advances in the theoretical basis for these models in recent years as discussed in section 8.2. One dimensional (column) models for atmospheric chemistry have traditionally been used for photochemical studies although advances in computing power have now made the 2 dimensional model more viable than in previous years. The hybrid nature of 1-d models - part local ,part hemispheric average - make interpretation and validation non-trivial, although this problem is generally ignored. The models' great strength lies in their use as a test bed for photochemical theories. One dimensional models are discussed further in section 8.4.

8.2. Photochemical model equations

In 3 dimensions the behaviour of the mixing ratio χ of a constituent gas is given by

$$\frac{\partial \chi}{\partial t} + \underset{\sim}{u}.\nabla\chi = P - L \qquad (1)$$

where P and L are photochemical production and loss terms, t is time and $\underset{\sim}{u}$ is the wind velocity. Reduction to 2 dimensions is acheived by taking the zonal average of Equation 1, defined by

$$\bar{X} = \frac{1}{2\pi}\int_0^{2\pi} X \, d\lambda$$

where λ is longitude.

This gives

$$\frac{\partial \bar{\chi}}{\partial t} + \overline{\underset{\sim}{u}.\nabla\chi} = \bar{P} - \bar{L} \qquad (2)$$

Problems arise with the representation of the 2nd term which can be expanded as

$$\overline{\underset{\sim}{u}.\nabla\chi} = \bar{\underset{\sim}{u}}.\nabla\bar{\chi} + \overline{\underset{\sim}{u}'.\nabla\chi'} \qquad (3)$$

where primes denote deviations from the zonal average. Assuming a non-divergent perturbation wind field, the last term can be written

$$\overline{\underset{\sim}{u}'.\nabla\chi'} = \nabla.\left(\overline{\underset{\sim}{u}'\chi'}\right) \qquad (4)$$

At this stage the right hand side of Equation 4 is separated into the local cartesian components and parameterised in terms of the zonal gradients of the species using an 'eddy diffusion matrix' such that

$$\begin{pmatrix} \overline{v'\chi'} \\ \overline{w'\chi'} \end{pmatrix} = - \begin{pmatrix} K_{yy} & K_{yz} \\ K_{zy} & K_{zz} \end{pmatrix} \qquad (5)$$

This basic approach was first suggested by Reed and German(1965) who assumed a symmetric matrix $K_{yz} = K_{zy}$. Holton(1981) has justified and improved this approach by writing the total transport as the sum of a symmetric and antisymmetric matrix. However it should be emphasised that the parameterisation is quite unable to represent accurately all aspects of transport by large scale planetary waves. Values of the K matrix have been determined empirically from dynamical and tracer studies and to a certain extent by fitting model results to observations. Improvements in the theoretical basis for 2-d modelling have come, however, from reinterpreting the zonal average wind field used in Equation 3 not as the Eulerian average but as the residual circulation of Andrews and McIntyre (1976). This more nearly represents the mass transport circulation than that obtained with the conventional Eulerian mean flow , as discussed in more detail in the Middle Atmosphere lectures.

One dimensional (column) models are obtained by averaging Equation 2 with respect to latitude. Using the same approach as for 2-d models the species conservation equation becomes

$$\left\langle \frac{\partial \chi}{\partial t} \right\rangle + \langle w \rangle \left\langle \frac{\partial \chi}{\partial z} \right\rangle = \langle P \rangle - \langle L \rangle + \frac{\partial}{\partial z} \left\langle \frac{\partial \chi}{\partial z} \right\rangle \qquad (6)$$

where the angled brackets denote hemispheric averages.

Species conservation equations (1,2 or 6) are solved for each species involving perhaps 50 or more equations. These are weakly coupled by the production and loss terms P and L , which are determined by considering a large number (perhaps 100 or more) of reactions of the form

$$A + B \rightarrow C + D \qquad (7)$$

From Equation 7 we can write, by the law of mass action

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} = k[A][B]$$

$$L_A = k[A][B] \qquad P_C = k[A][B]$$

where k is a measured rate constant and in general is a function of temperature of the form

$$k = \alpha \exp(-\beta/T)$$

In principle, models calculated averaged quantities for P_C and L_A which include correlation terms of the form $k\overline{[A]'[B]'}$. In practice, these terms are ignored i.e.

$$\overline{P}_C = k\overline{[A]}\,\overline{[B]}$$

although this may lead to error under some circumstances. Square brackets denote concentrations in molecules per unit volume. The total loss of species A is determined by adding all the loss rates for all the reactions of the form of Equation 7 with A appearing on

the left hand side. Likewise the total production of C is computed from all the reactions of the form of Equation 7 with C appearing on the right hand side.

Numerical techniques for solving these equations vary depending on the type of modelling (1-d,2-d or 3-d) and the timescales that are of interest. There is insufficient space to discuss this at length, but, briefly, problems arise because the system of differential equations is 'stiff' , that is has a wide range of timescales from fractions of a second to months. As an example , the trajectory method, which dominates the Met. Office's current research in atmospheric chemistry modelling, is concerned with timescales up to about 10 days and the finite difference scheme to solve the equations has a timestep of 30s during daylight reducing to 1s at sunrise and sunset.

8.3. The comparison of models and data

To have some confidence in the models which are used to study both the current atmosphere and to make predictions about its future development, comparisons between models and data are required. In this section types of comparison are discussed. These vary considerably in there usefulness for testing various aspects of model behaviour.

It is common to compare modelled and observed vertical profiles of constituents, although this is not always easy to interpret. For example, the 20%

underprediction of ozone in the upper stratosphere of most models is thought to constitute 'poor' agreement while factors of two in comparison between modelled and measured OH are considered 'satisfactory'. Further, one and two-dimensional models are incapable of modelling the specific dynamical conditions appropriate to a given observation. Thus any discrepancy could be due to inadequately modelled transport or chemistry and the comparison does not constitute an accurate test because it cannot isolate the relevant physical processes.

One possible test is to compare modelled and measured ratios of critical species which should be in balance. For example, in photochemical equilibrium the NO to NO_2 ratio is given by

$$\frac{[NO]}{[NO_2]} = \frac{J_{NO2} + k_1[O]}{k_2[O_3] + k_3[HO_2] + k_4[ClO]}$$

where the k's denote reaction rates and J_{NO2} is the dissociation rate of NO_2. However, from this equation, Harries(1982) has shown that the ratio can only be tested to an accuracy of about 30% with current measurements of the appropriate concentrations and rates. Since NO and NO_2 play a major role in ozone destruction in the stratosphere this level of accuracy is insufficient to constrain significantly atmospheric models.

An extremely informative test, with less stringent measurement requirements is the comparison of diurnal variations. Since it is the relative diurnal changes which are important the observations need only

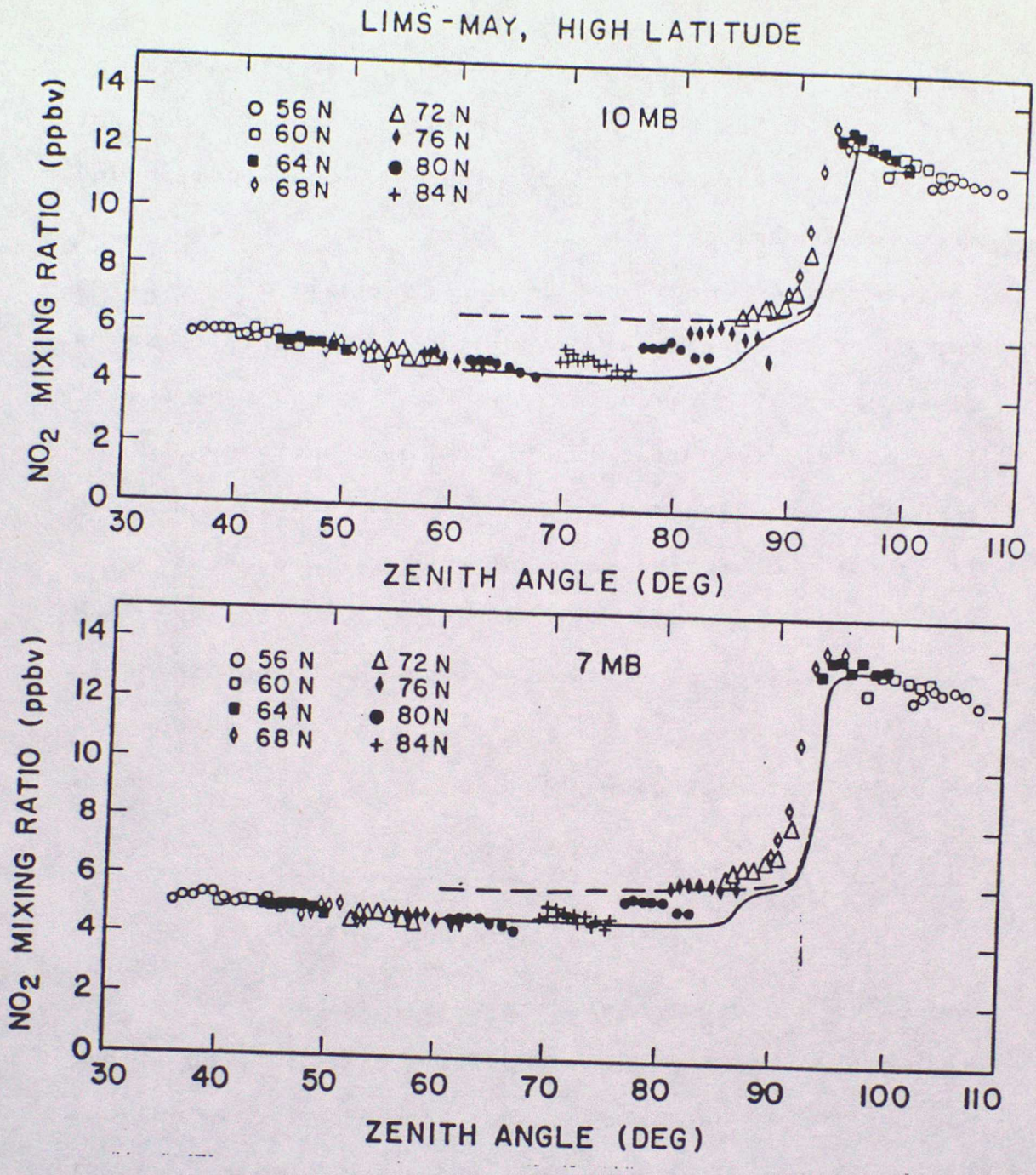


Figure 1. Observed variation in NO_2 mixing ratios at latitudes from 56° to 84°N during May, as a function of zenith angle, zonally and 4-day averaged at the 10mb and 7mb levels. The dashed line is the model result from Solomon et al. (1986) assuming pure adsorption, single scattering. The solid line is that obtained for a columnar multiple-scattering model with an albedo of 0.3.

have high precision with the absolute accuracy being relatively unimportant. An example showing the usefulness of this approach is given in Figure 1 which shows model results and satellite observations for NO_2 in the stratosphere (Solomon et al.,1986). Nitrogen dioxide is approximately constant during the daytime but increases rapidly at sunset, which at 10mb occurs when the solar zenith angle reaches about 95°. After sunset NO_2 decreases steadily due to N_2O_5 formation by the reactions R1 and R2.

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad R1$$

$$M + NO_3 + NO_2 \longrightarrow N_2O_5 + M \qquad R2$$

These results are well reproduced by the model calculations except that the rapid increase occurs earlier in the model than in the data. However, the satellite instrument has a horizontal resolution of about 500km and at sunset scans across the terminator so that observations assigned to night-time may contain a proportion of daytime NO_2. Consequently this model discrepancy is not considered significant.

Pallister and Tuck(1983) have suggested a role for high precision measurements of diurnal variations. Figure 2 shows the relative variation of ozone at altitudes between 40 and 50km. The diurnal variations change significantly with height due to the importance of different catalytic cycles. Measurements of these variations might be useful for assessing our understanding of upper stratospheric photochemistry.

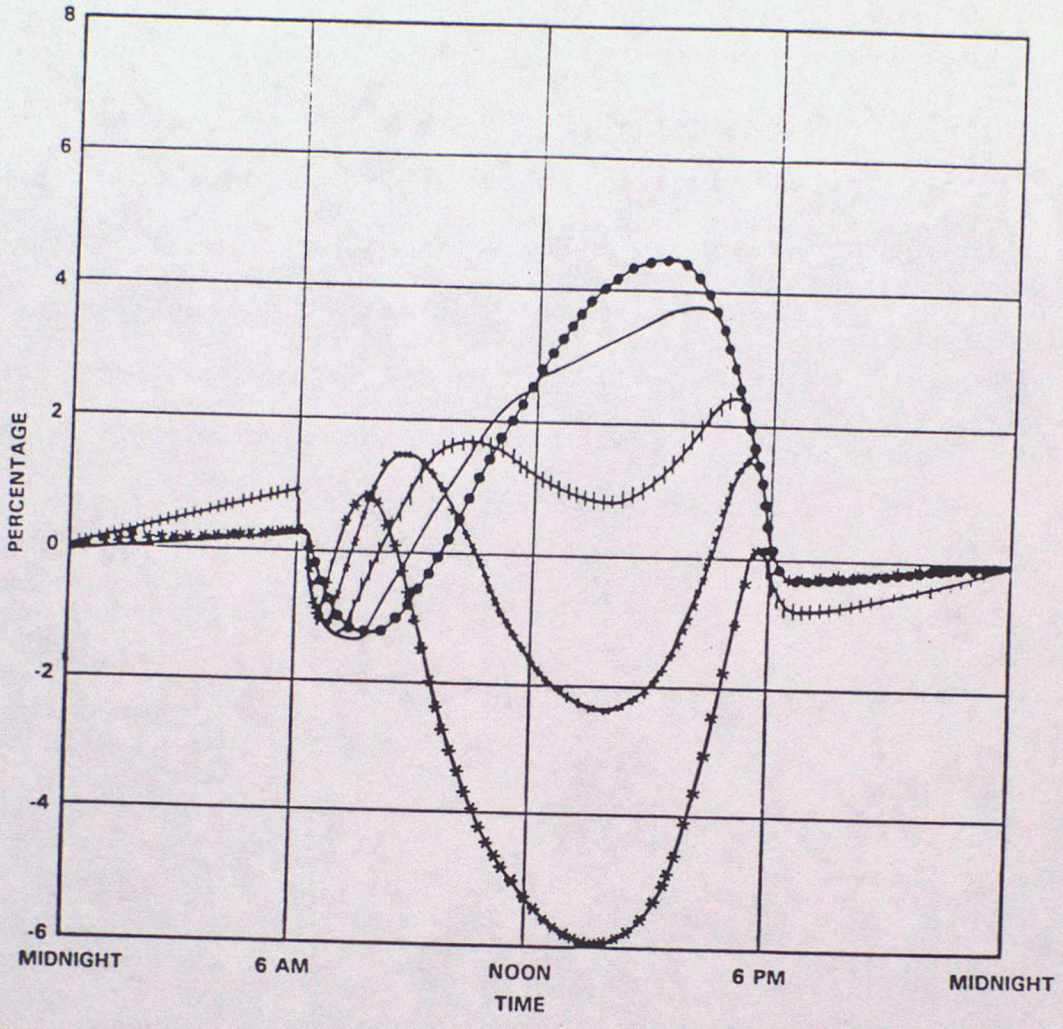


Figure 2 . Percentage deviation from midnight values of ozone concentrations for a diurnal cycle. Key: ● ≡ 40 km; — ≡ 42 km; | ≡ 44 km; X ≡ 46 km; × ≡ 48 km. From Pallister and Tuck (1983).

However, it should be pointed out that Pallister and Tuck's calculations were performed on constant density surfaces and it might be expected that diurnal temperature variations would contribute several percent to the ozone change via induced motions.

8.4. 1-D Models.

One dimensional coupled transport and kinetics models have been one of the basic tools in theoretical studies of the atmosphere. In particular, studies of the effects of anthropogenic pollution on stratospheric ozone have been done with the aid of one-dimensional models which solve Equation 6 for each species χ. The diffusive treatment of transport in a 1-d model is a purely empirical treatment based on the observations of the temporal and spatial distributions of selected tracers such as CH_4 and N_2O and radionuclides from past nuclear tests. While adopted profiles differ by as much as an order of magnitude at some altitudes these profiles tend to have similar characteristics: large values in the troposphere, much reduced values in the region near the tropopause, and increasing with altitude in the stratosphere. Generally, a single profile is chosen to represent transport of all species in the atmosphere. In practice, the representation of transport in the 1-d model has been limited by the lack of well-determined, globally averaged tracer data and by uncertainties in understanding their sources and sinks. Dynamically based transport parameterisations

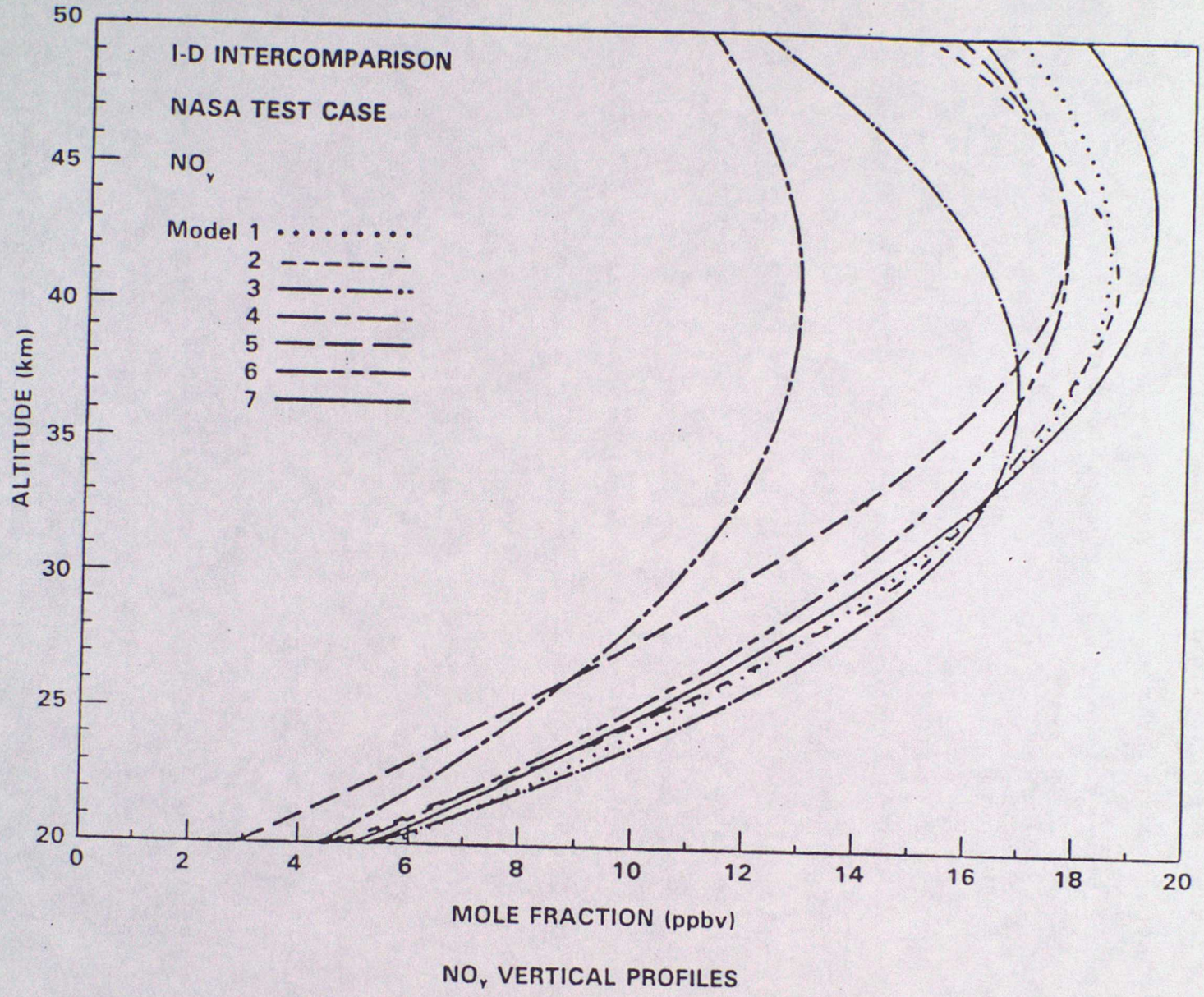


Figure 3. Intercomparison of NO_y vertical profiles for a range of 1-D models. From WMO(1986).

have been proposed in which K_{zz} depends on species and chemical gradients (Holton,1986). Although not fully developed and exploited these techniques may provide a better physical basis for representation of hemispherically averaged transport in 1-d models.

A further limitation of 1-d models is that it is difficult to average accurately the hemispheric rates for photochemical production and loss. Only local variables, such as solar flux intensity and temperature can be used. This complicates the interpretation of 1-d model results and has led to much discussion on the interpretation of calculated distributions of various species. Despite these difficulties the 1-d model captures many of the important features of trace gas behaviour in the atmosphere and remains a useful theoretical tool.

In the remainder of this section examples of the use of 1-d models will be shown. Firstly, some idea as to the differences between individual models is given in Figure 3 which shows 'total odd nitrogen' ($NO + NO_2 + HNO_3 + 2*N_2O_5$) predicted by a range of 1-d models. Note that the qualitative form is similar in all cases with a broad peak at about 40km with model 3 predicting a peak some 5km lower in altitude. However the value of the peak varies from about 13ppbv to about 19ppbv, largely due to differences in the calculated photolysis rates of N_2O and NO. In comparison, satellite data from the LIMS instrument indicates a peak of about 20ppbv. This illustrates a severe weakness in our current knowledge because ozone

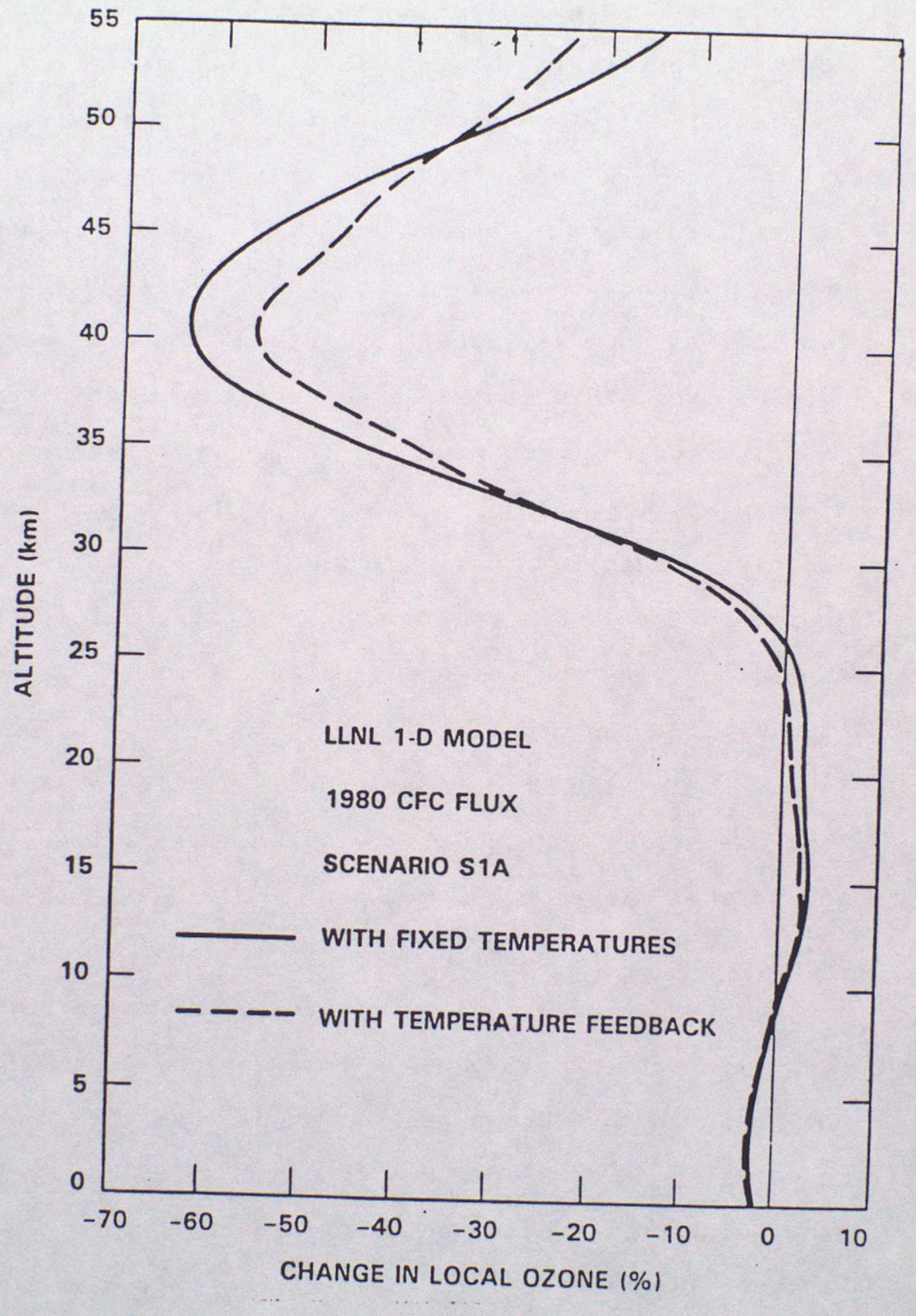


Figure 4. Steady state change in local ozone in a 1-D model, assuming continued CFC fluxes at 1980 levels.

destruction in the present stratosphere is dominated by the odd nitrogen catalytic cycle. Also, odd nitrogen plays a role in the formation of reservoir species (e.g. HNO_3, $ClONO_2$) which therefore affects the odd hydrogen and odd chlorine catalytic cycles. In the upper stratosphere ozone changes are dominated by Chloro-Fluoro-Carbons (CFCs) which are produced in the troposphere and dissociate in the upper atmosphere releasing chlorine radicals which catalytically destroy ozone. An example of a 1-d model prediction of this effect is shown in Figure 4. The results illustrate steady state calculations due to continued emmission of CFCs at 1980 production rates. Note the substantial reduction in the upper stratosphere compared with a slight decrease in the troposphere and a slight increase in the lower stratosphere. The last point illustrates the 'photochemical self healing' property in which destruction of upper atmospheric ozone causes increased penetration of UV radiation to lower levels where more ozone can be formed by reactions R3 and R4.

$$O_2 + h\nu \longrightarrow O + O \qquad \text{R3}$$

$$M + O + O_2 \longrightarrow O_3 + M \qquad \text{R4}$$

Other pollutants can strongly affect the O_3 concentration. Figure 5 shows the effect on ozone of doubling the concentration of CH_4 alone and Figure 6 shows the effect of doubling CO_2 alone. The effect of methane is largely chemical and acts by reaction R5 to reduce the effectiveness of the chlorine catalytic

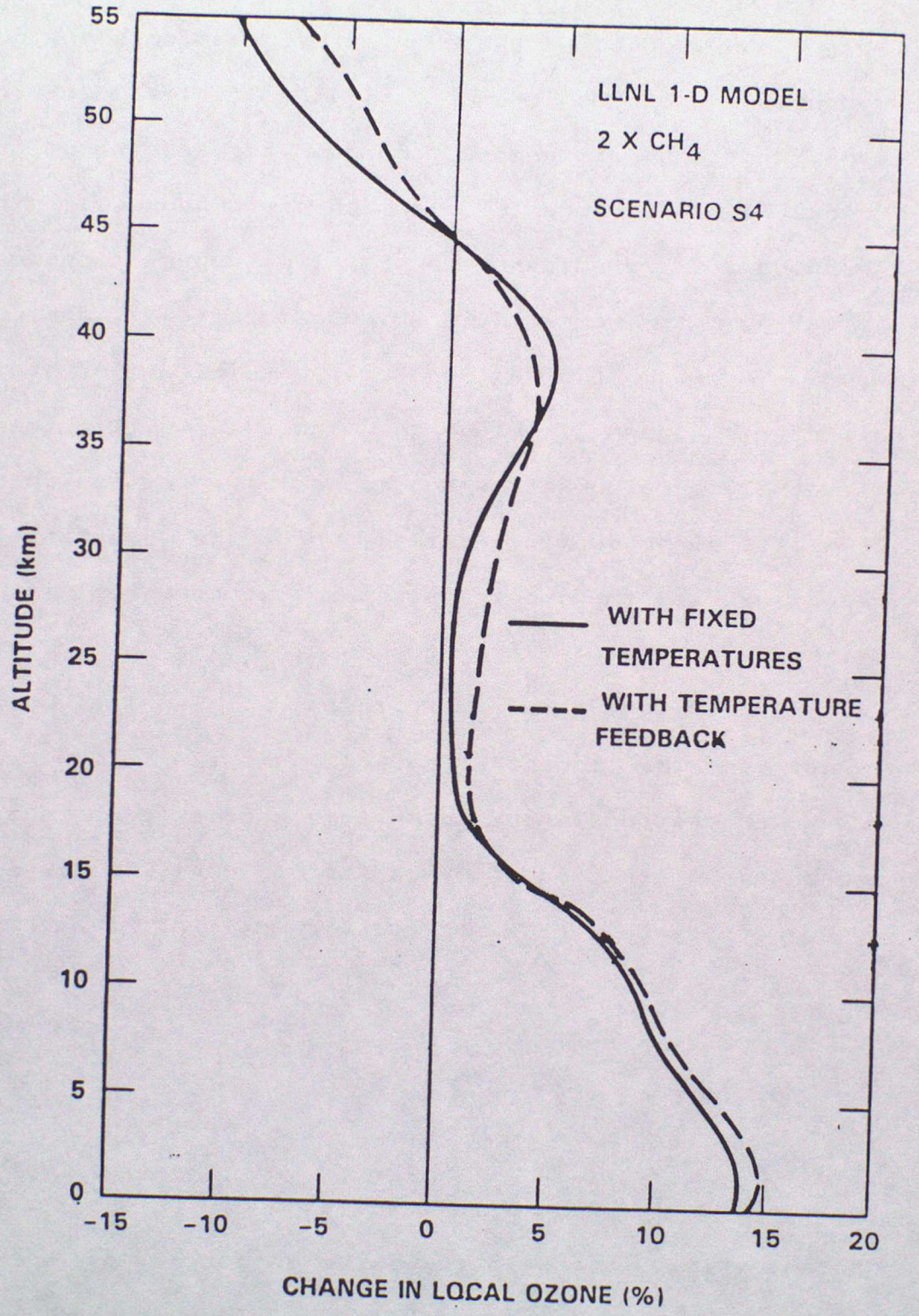


Figure 5. Calculated percentage change in local ozone as a result of doubled atmospheric methane.

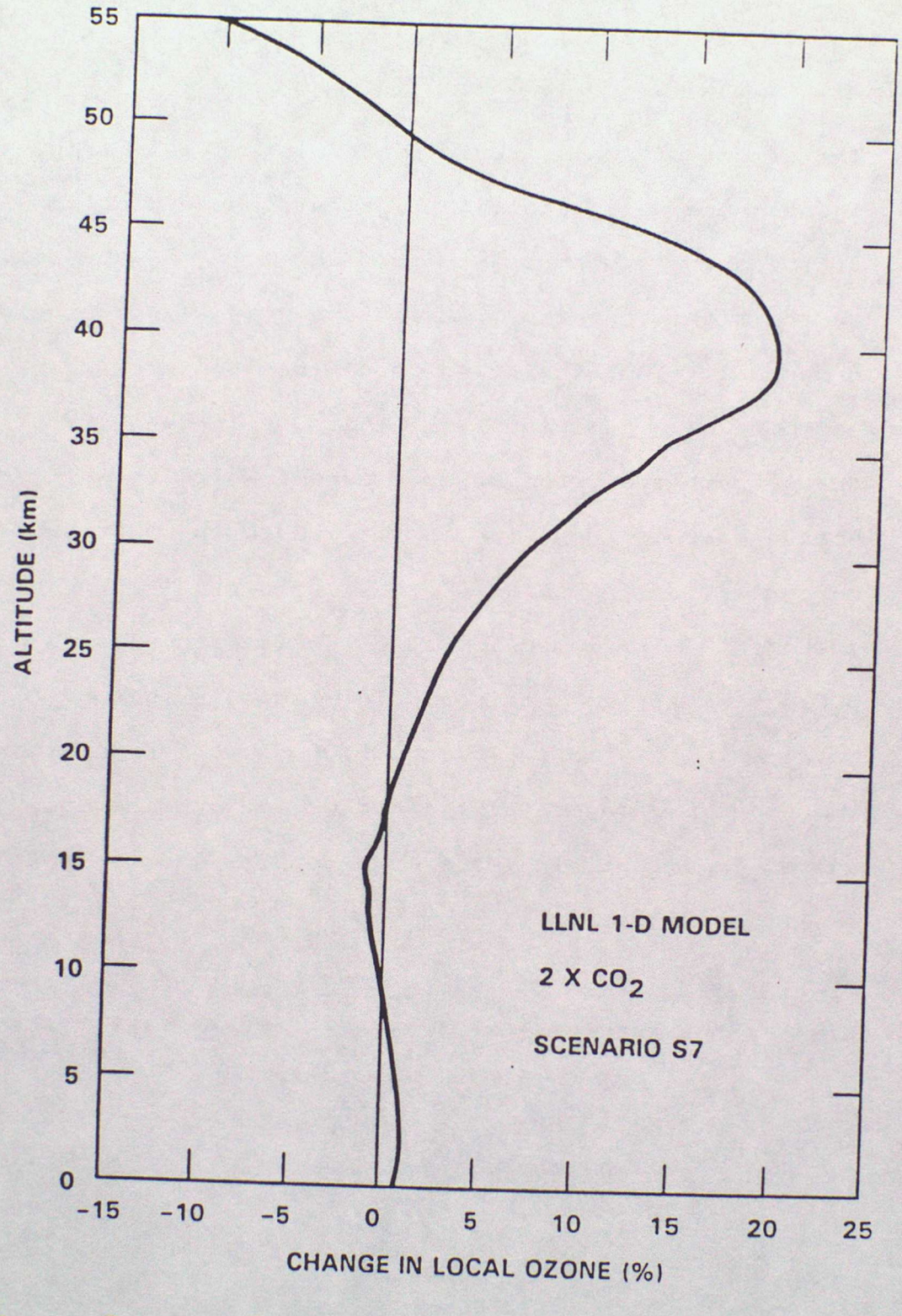


Figure 6. Calculate. percentage change in local ozone for doubling of carbon dioxide.

cycle by forming HCl which acts as a long lived reservoir for chlorine.

$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad R5$$

The effect of CO_2 is radiative. Higher CO_2 warms the troposphere while cooling the stratosphere. Cooling the stratosphere decreases the effect of the ozone destruction mechanisms which are highly temperature dependent. Thus the ozone concentration increases. An example of a pollutant which has its largest effect in the troposphere is given in Figure 7 which shows steady state calculations for an increase in CH_3Br surface concentration from present day values of 20pptv to 100pptv. This molecule is dissociated or reacts with OH to form active bromine molecules. In general the bromine catalytic cycle is 10-100 times more efficient than the chlorine catalytic cycle so bromine may be quite important in the future despite its vanishingly small concentration.

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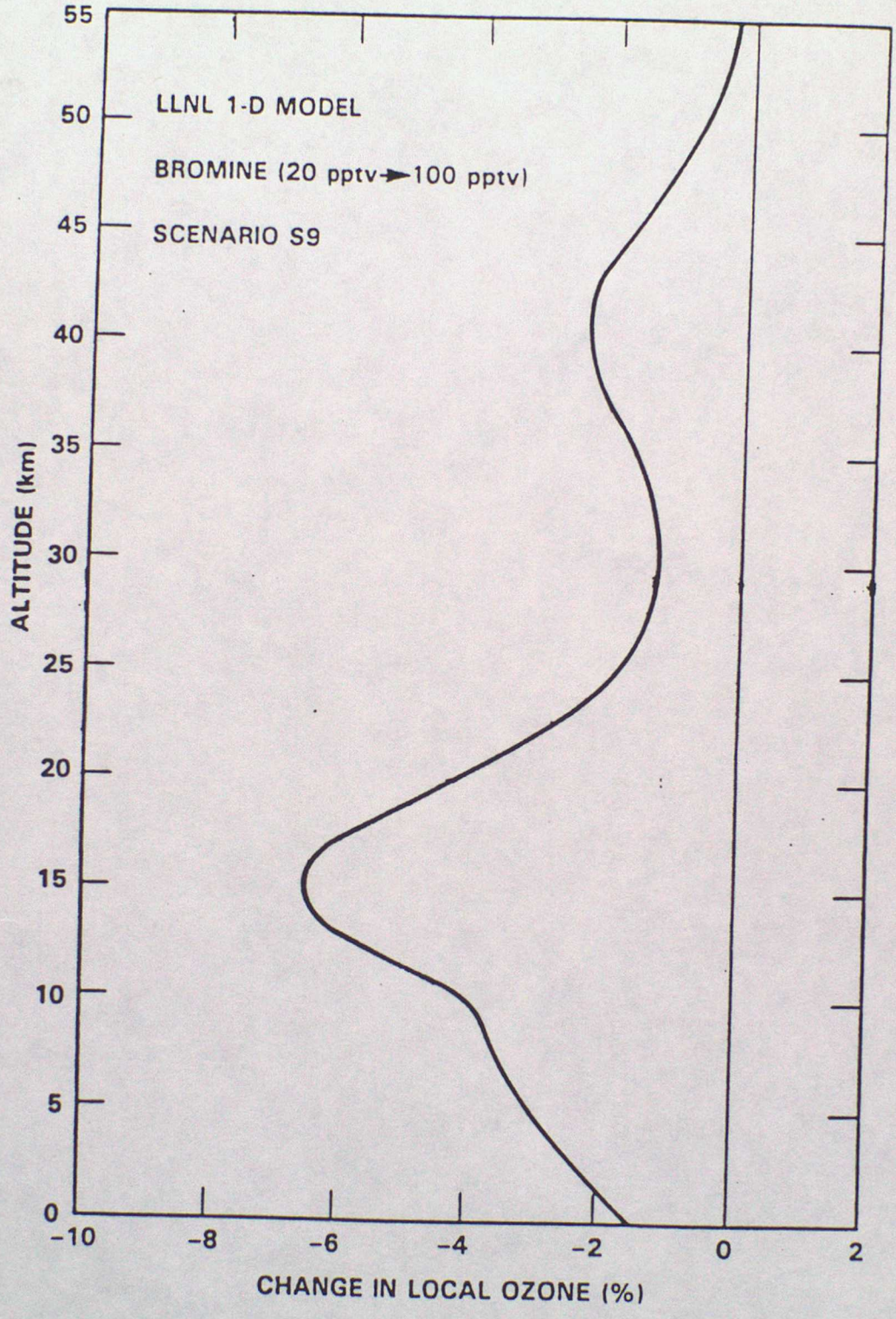

Figure 7. Calculated percentage change in local ozone when surface CH_3Br concentration is increased from 20 to 100 pptv.

In the next lecture results from 2-d and 3-d models and trajectory models will be discussed. For general references WMO(1986) may be consulted and for more specific items the following references may be studied.

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Lecture 9: Models of Atmospheric Chemistry II

by Dr. J.Austin

9.1. 2-d models

The chief advantage of 2-d models over 1-d models is the ability to simulate latitudinal and seasonal variations of long lived trace species such as N_2O and CH_4. However, there are many differences in the results obtained according to the different types of advection and diffusion schemes employed. Long-lived trace gases with sources in the troposphere, such as N_2O, are injected primarily in the tropics. As the tropical air parcel is transported upward by the mean circulation, destruction of source species occurs by photolysis or reactions with $O(^1D)$ and OH. Destruction continues as the parcels are advected poleward in the stratosphere and the parcels then descend at high latitudes with lower concentrations of the source gases. The source gas mixing ratios are thus greater at the equator than at the poles.

Figure 1 shows examples of model predictions of N_2O for July. The Dupont model has large eddy diffusion. The NOCAR model is a 'residual circulation' model mentioned briefly in the previous lecture and the GSFC model uses a diabatic circulation to advect the

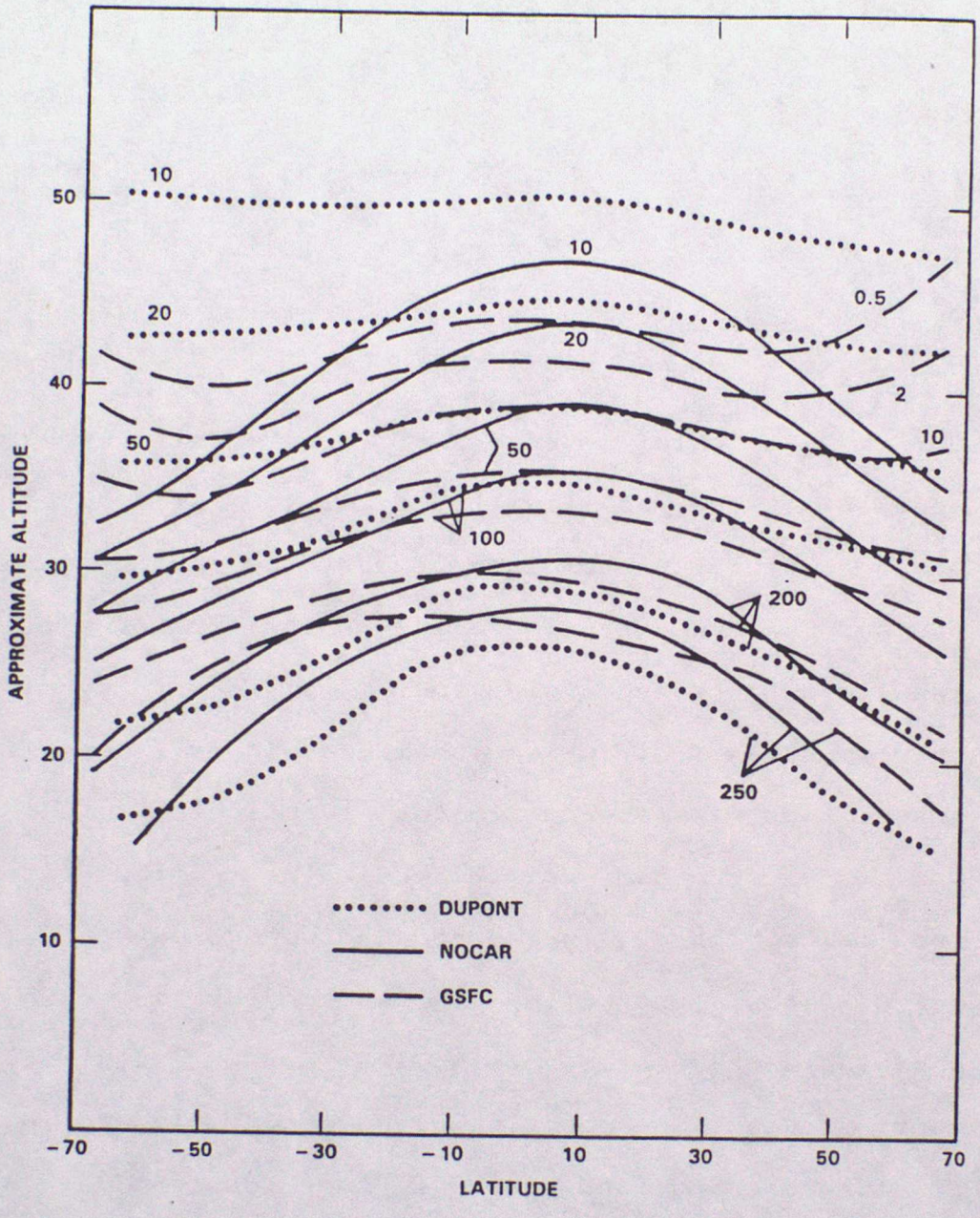


Figure 1 Latitude-height cross-section of the N_2O distribution (ppbv) from three different 2-D models.

constituents. The advective models (GSFC,NOCAR) give larger downward-sloping gradients in the contours at low and mid-latitudes. The NOCAR model in particular strongly mirrors the underlying equator to pole circulation.

An interesting feature of the satellite observations of N_2O is the presence near equinox of local minima in mixing ratio at the equator with maxima in the sub-tropics. This is in contrast to the usual situation with a single low latitude maximum. Jones and Pyle(1984) discussed this feature in detail, known as the 'double peak' structure, and were unable to simulate it with a 2-d model. Using the same model but with improved representation of dynamics Gray and Pyle (1987) have now partially modelled the feature (Figures 2,3). They hypothesise that it is related to the low latitude semi-annual oscillation and gravity wave drag. The westerly phase of the semi-annual oscillation has descending motion at the equator, sufficient to produce the local minimum there. The model also reproduces somewhat similar features in CH_4 and O_3 and leads to an improved low latitude seasonal variation.

Despite these successes with 2-d models, there are still problems in the treatment of transport in the equatorial lower stratosphere or upper troposphere. In this region the radiative heating is the small, poorly defined difference of small heating and cooling terms. However, an accurate nett heating rate is required to calculate the flux of source gases into the mid-stratosphere.

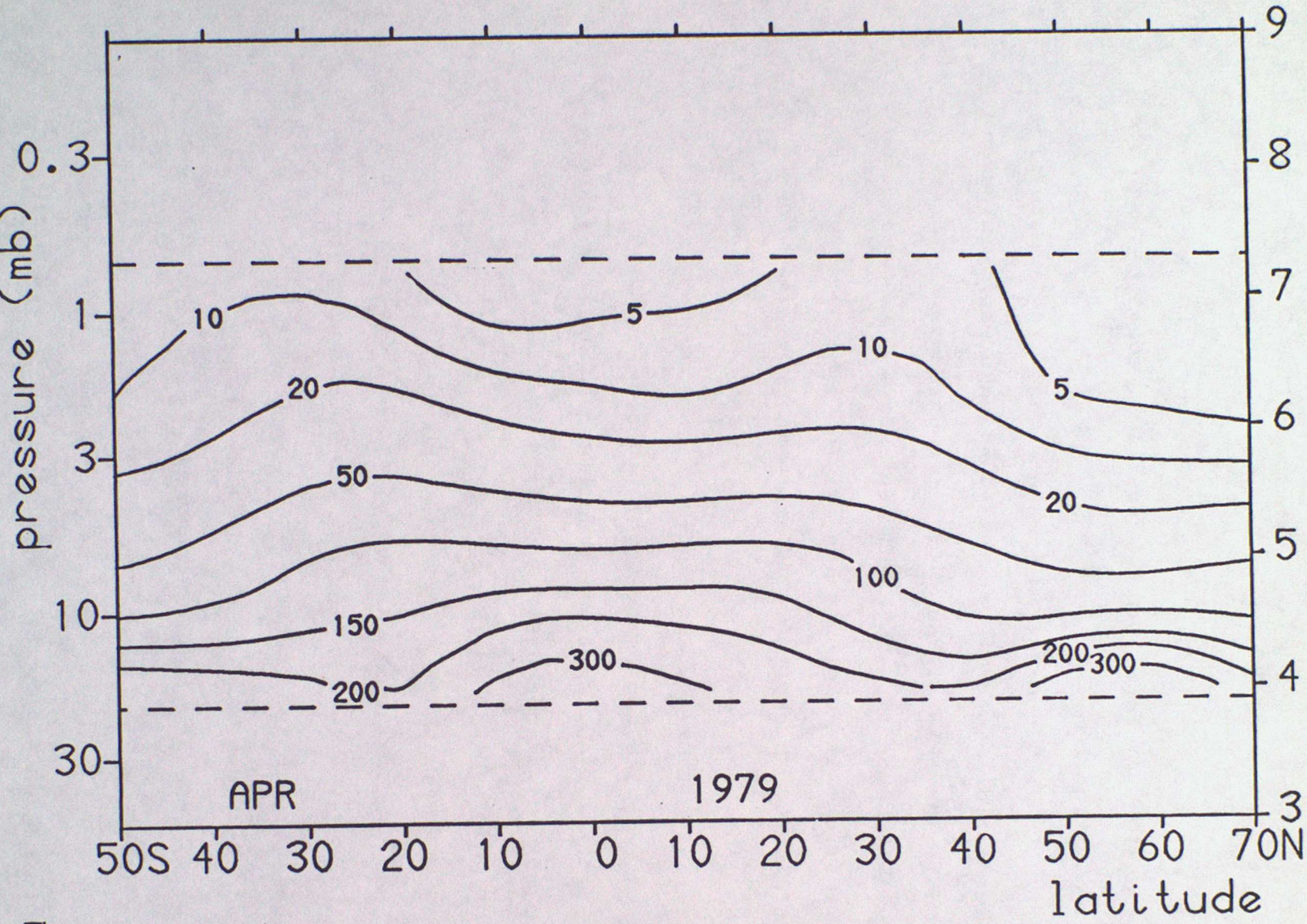


Figure 2. Monthly mean N_2O concentration from SAMS for April 1979. Taken from Jones and Pyle (1984). Concentrations are in ppbv.

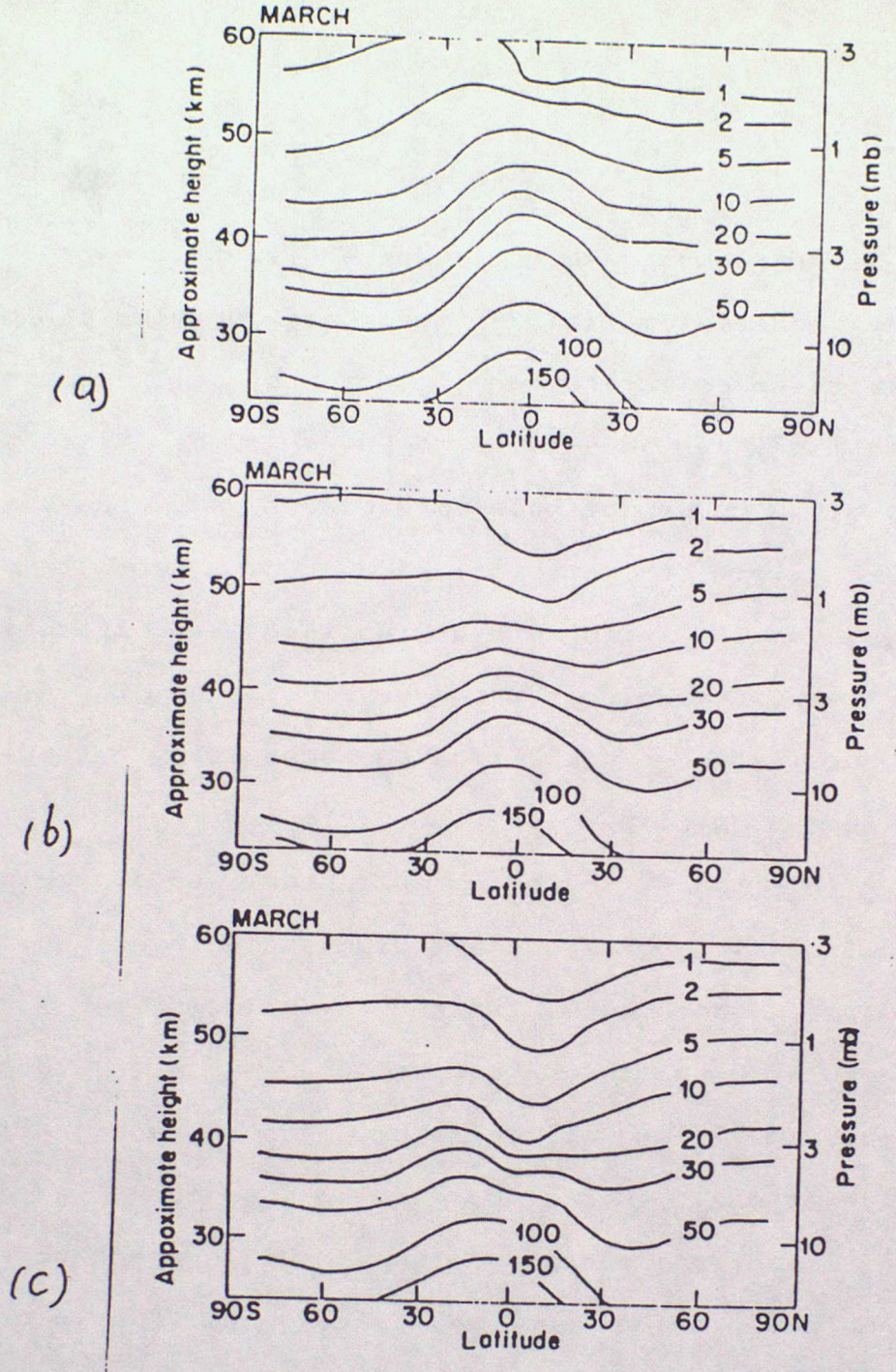
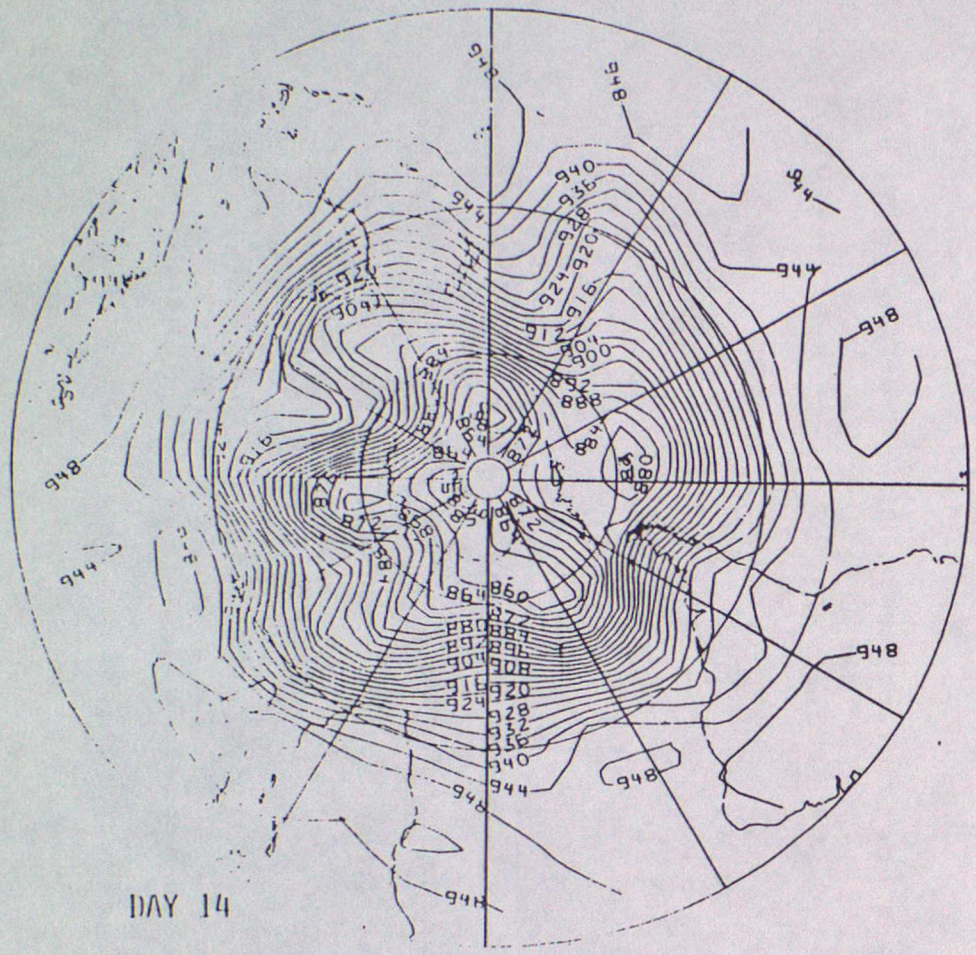


Figure 3. Monthly averaged latitude-height cross-sections of N_2O volume mixing ratio (ppbv) for the month of March, taken from Gray and Pyle (1987). (a) Standard model (b) model with gravity waves but no SAO (c) model with gravity waves and SAO.

9.2. 3-d models

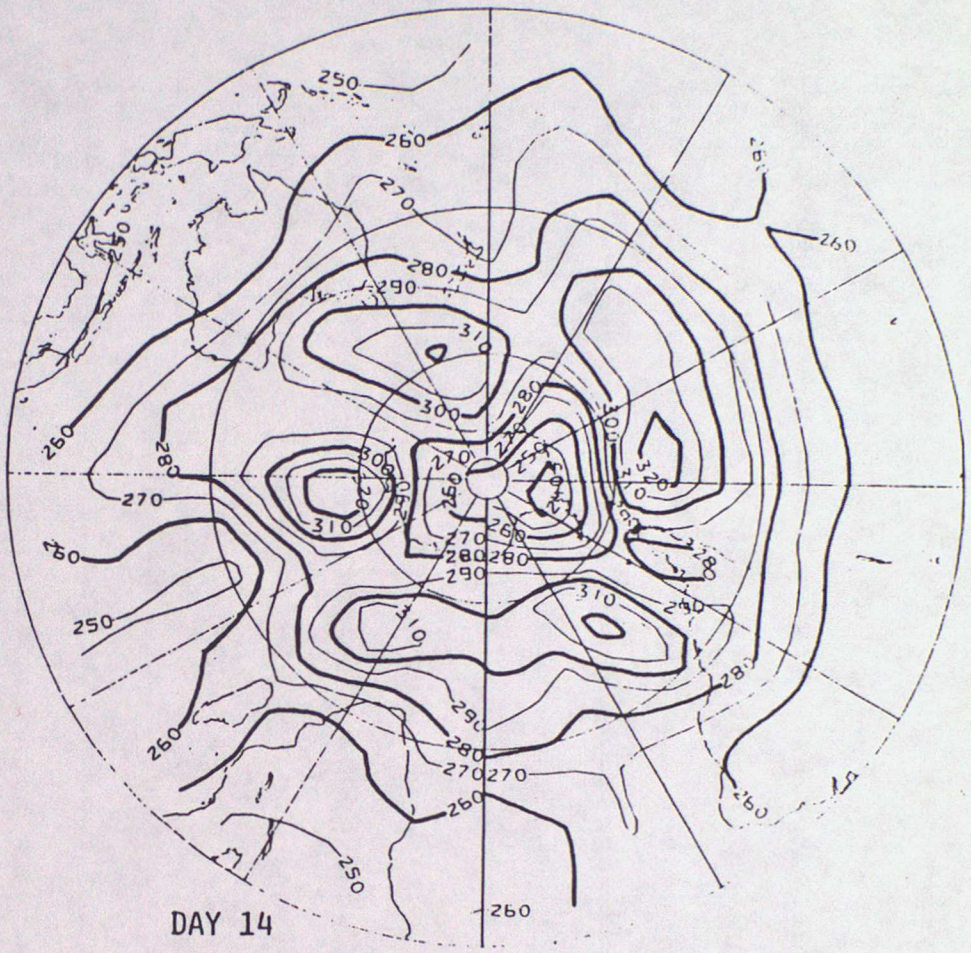
3-d models have the supreme advantage over 1-d and 2-d models in that atmospheric dynamics can be fully represented but suffer in that not all species concentrations can be held in computer memory at any one time. A number of models have been developed over the years (e.g. Mahlman et al.,1980) which consist of GCM type models with one or two long lived tracers. Another type of model has been developed by Cariolle and Déqué(1986) in which ozone photochemistry has been linearised using relaxation times inferred from a 2-d model. In their Southern hemisphere study, the dynamical model generated the medium scale waves which are often observed. These waves tend to form quasi-regular O_3 patterns (see figure 4) with zonal wavenumbers 4,5 and 6, in fairly good agreement with the observations. This study gives a good illustration of the important role played by GCMs in understanding the interactions between dynamical and physical processes in the troposphere and wave activity and O_3 distribution in the lower stratosphere. However, the model does not simulate the Antarctic ozone decrease as discussed in an earlier Atmospheric Chemistry lecture.

An alternative type of 3-d model (Grose et al.,1987) incorporates chemistry by grouping certain species together into families, as described briefly in Atmospheric Chemistry lecture 4. This family concept partitions the species into groups so that, although



GEOPOTENTIAL - 300 MB -

Fig. 4a



TOTAL OZONE

Fig. 4b

Fig. 4 (*a*) The 300-mbar geopotential field (in decameters) and (*b*) the total ozone distribution (in Dobsons) for day 14 of the simulation where the medium-scale wave with a predominant wave number 5 has a large amplitude.

Taken from the 3-D model simulation of Cariolle and Déqué (1986)

there may be rapid chemical conversions between individual members of the family, the characteristic lifetime of the family is long in comparison to that of the individual species. Having determined the total concentration of each family, the concentrations of the individual members may be determined using chemical equilibrium expressions, such as the NO/NO_2 ratio discussed in the previous lecture. Grose et al. conducted a 5 month simulation by transporting O_x, NO_y, Cl_y and HNO_3. THe results of the simulation were quite encouraging when compared with satellite data. However, the simulations shared defficiencies common to most model studies of the stratospheric ozone distribution. In particular, the ozone mixing ratio is lower than observed in the upper stratosphere and the nitric acid maximum in winter high latitudes is underpredicted (see also Austin et al.,1986). These features appear to be associated with defficiencies in our understanding of the chemical mechanisms involved : rate coefficients, spectroscopic data or some combination thereof.

9.3. Trajectory models

Much of the Met.Office's current Atmospheric Chemistry modelling research involves the use of trajectories. In this technique air parcel trajectories are computed from observations and the chemical equations are integrated along them. For this technique to be successful, we rely more than in other modelling methods on both dynamical and chemical

observations of the atmosphere. The technique is well suited to a direct comparison between model results and local chemical observations and does not suffer from the criticisms of 1-d and 2-d models in this regard.

To calculate trajectories in the stratosphere horizontal winds are obtained by applying the gradient wind relation to satellite derived geopotential height fields (Austin and Tuck,1985). To a good approximation, over 10 days or so, stratospheric trajectories are isentropic but since chemical reaction rates are sensitive to the local concentrations and hence density, a further adjustment is applied using a radiative correction to the isentropic surface. The use of a radiative correction allows the vertical component of the wind velocity to be implicitly incorporated. Trajectories can also be calculated directly from the wind fields assimilated in analyses of the troposphere. Examples of trajectories calculated for the mid-stratosphere during a stratospheric warming are shown in Figure 5. These trajectories were computed for the period 21 February to 3 March 1979, after the circumpolar vortex had split into two separate vortices. The trajectory starting at 70°N in the Eastern vortex completed several circuits by the end of February. In contrast, the trajectory starting at 80°N and the same longitude transferred to the Western hemisphere after just one circuit of the Eastern vortex.

The quality of the trajectories that can be obtained varies substantially according to the

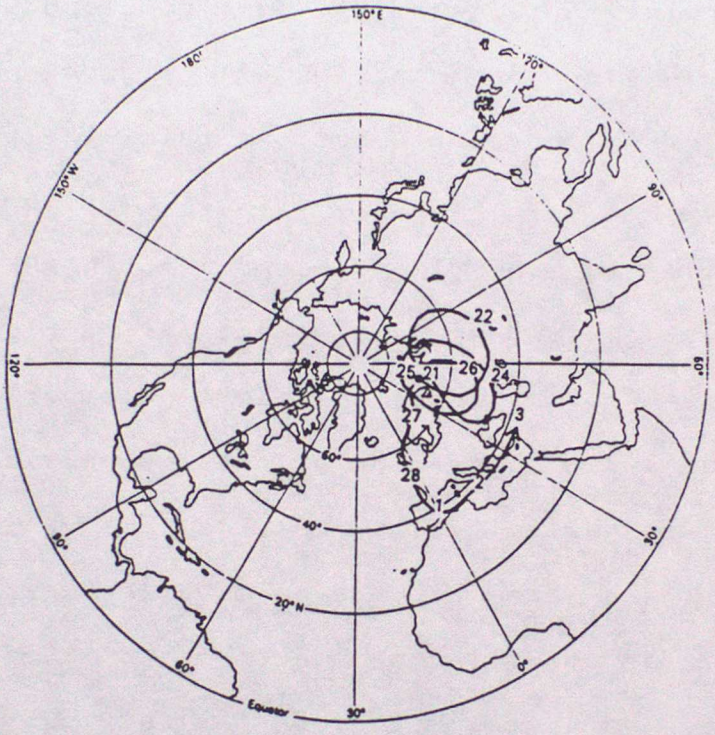
Figure 5 Examples of trajectories starting at the 850K potential temperature surface on 21 February 1979. The number along the trajectories are the dates

(a) Trajectory starting at 70°N, 50°E

(b) ..... 80°N, 50°E

Taken from Austin and Tuck, 1985.

(a)



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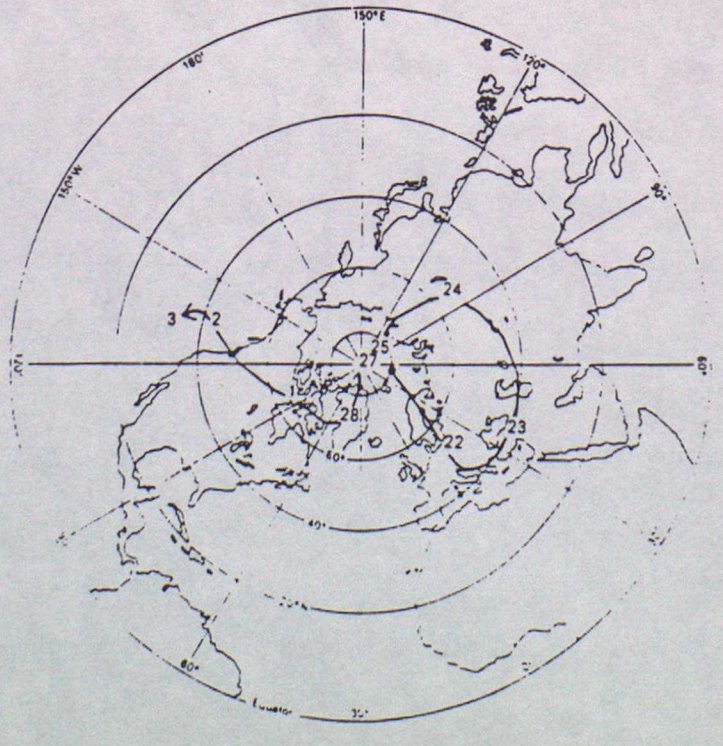


dynamical conditions. A trajectory starting in a quiescent part of the atmosphere, for example in the centre of the Aleutian high, will probably remain accurate for about 10 days. On the other hand a trajectory starting in a disturbed, rapidly evolving part of the atmosphere, such as the trajectories illustrated in Figure 5, may be quantitatively reliable for only 3 or 4 days. Thus the usefulness of chemical modelling along trajectories is limited to about 10 days.

To integrate the chemical equations along the calculated air parcel trajectory Equation 1 of lecture 8 is used, written in Lagrangian form

$$\frac{D\chi}{Dt} = P - L$$

The terms P and L are determined by the pressure and temperature of the parcel (to determine the reaction rates), and by the solar fluxes incident on the parcel (to compute the photodissociation rates). The temperature and pressure of the air parcel are supplied directly from the trajectory coordinates. The solar fluxes are computed using a radiative model which requires the solar zenith angle (calculated from the trajectory coordinates) and the ozone profile (taken from satellite observations). Note the reliance of the chemical calculations on coincident observations of ozone and, in principle, other radiatively active gases. Thus, the trajectory method should be viewed as a technique for interpreting rather than predicting

chemical concentrations. Further details of the technique may be obtained from Austin et al.,(1987).

The chemical model used for stratospheric work currently contains 40 species and 105 reactions. Even with the best available composition dataset (4 species from the LIMS instrument and 2 from the SAMS instrument), the concentrations of many species are unconstrained. However, in practice, the radical species have such low concentrations and short photochemical time-scales that they may be initialised to zero and quickly become established within the model. Nonetheless, there are several species, mostly reservoir species such as $ClONO_2$, N_2O_5 and HCl which may require careful consideration. Also, those measurements that we do have are subject to systematic and random errors so that in practice initialisation of the chemical model is difficult. Figure 6 shows the results obtained (Austin and Butchart,1987) for the chemical model integrated along a trajectory in late January 1979 together with observations from the LIMS satellite instrument. For this trajectory agreement within observational error was obtained between model and observations for all LIMS species. On the other hand for another trajectory in late January the model does not agree with LIMS observations (Figure 7).

These results expose many of the difficulties of trajectory modelling. Note the large scatter in chemical observations compared to a typical change in model concentration. This implies that along a single trajectory photochemical conditions need to change

Figure 6 Chemical model run along trajectory starting at the 850K potential temperature surface on 27 January 1979. The solid lines are the model results, the circles are LIMS satellite observations and the broken lines are linear regression lines through the data. The air parcel peels from the circumpolar vortex.

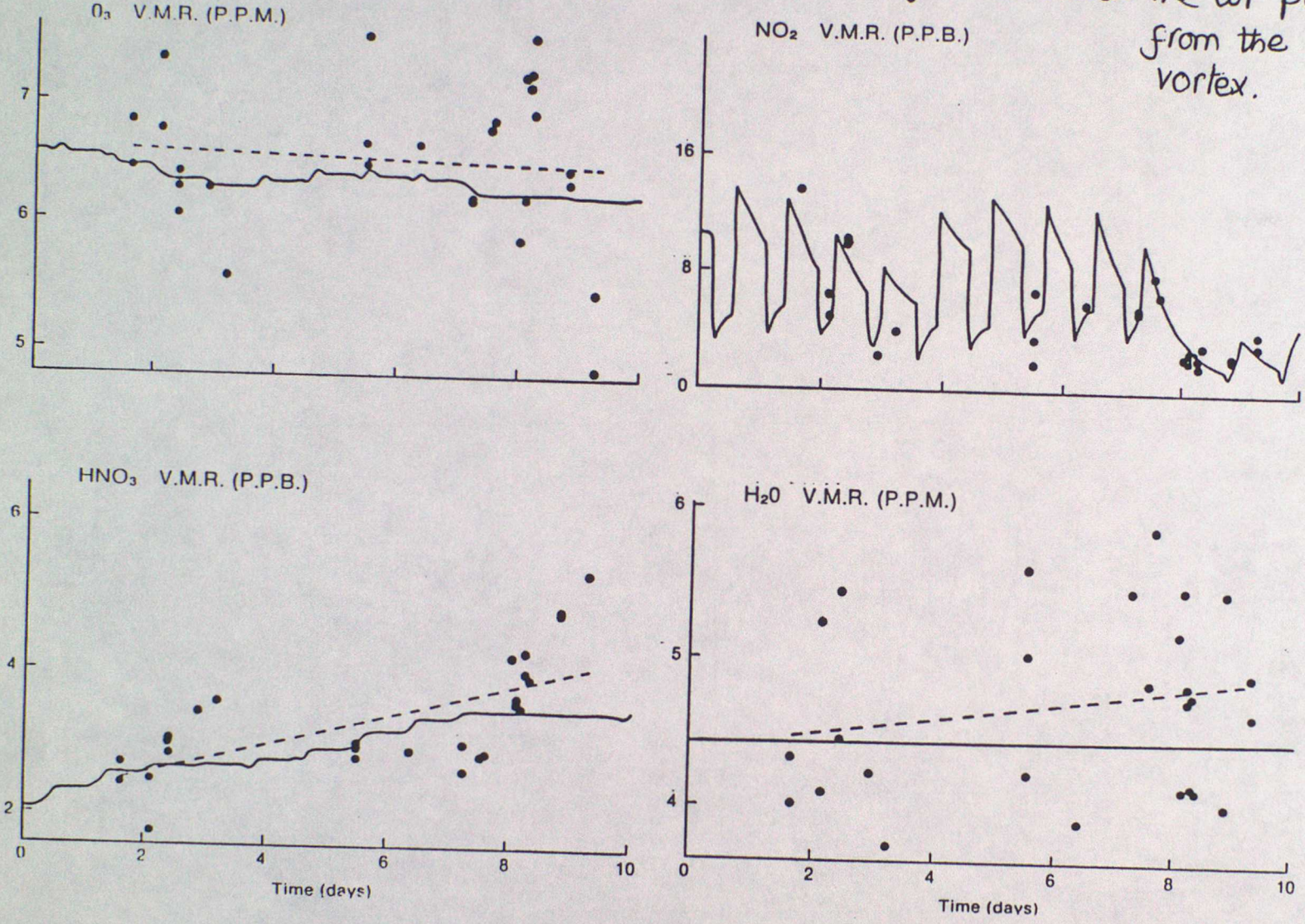
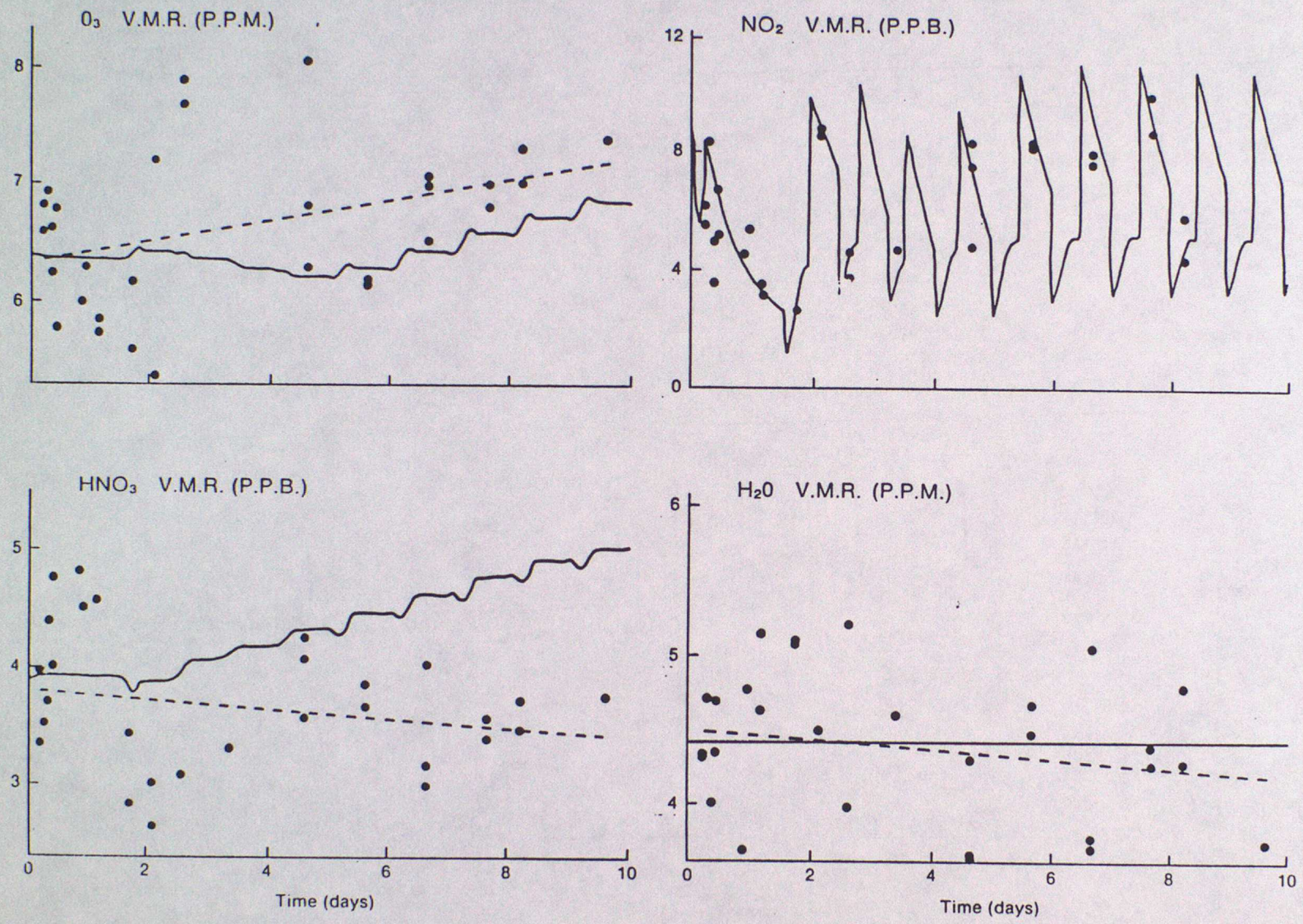


Figure 7 Chemical model run along trajectory starting at the 850K potential temperature surface on 27 January 1979. Notation as Figure 6. The air parcel is transported to the tropics.



substantially to produce a statistically significant change in observed concentration in 10 days. The examples chosen have large latitudinal excursions during a stratospheric minor warming and even under these conditions careful statistical analysis of the results is required. The approach suggested by Austin and Butchart(1987) is to perform calculations along groups of 5 or more trajectories with similar physical characteristics and by averaging the results, the statistical noise can be reduced. These results suggest that there may be good physical reasons as to why the model agrees with observations in some cases but not in others. The original purpose of doing trajectory modelling was, in some sense, to isolate the importance of chemistry from that of dynamics; these latest results suggest that under some circumstances this is not possible. The difficulties of trajectory modelling in the troposphere are in many ways more extreme. The volume of satellite data available in the stratosphere means that at least for limited periods, simultaneous computer experiments can be performed which produce a large sample to carry out statistical manipulations. In the troposphere, it takes a lot longer to produce a large sample of observations and, further, trajectories are less reliable because of the larger effect of transients and small scale dynamical processes, unrepresented in the analyses.

9.4. Tropospheric modelling

All the above techniques are, of course, equally applicable to both stratosphere and troposphere although the increased complexity of the chemistry in the lower atmosphere means that even 2-d modelling is barely practical with current computing power. In these lectures I have concentrated on the stratosphere because it provides a wider range of modelling techniques but in this section I will present briefly some tropospheric work in progress at UKAEA Harwell (Derwent and Hough,1986).

As mentioned in previous lectures much of the interest in tropospheric chemistry has arisen from the need to understand the effect of anthropogenic pollution. The ozone concentrations in the UK , for example, sometimes exceed levels at which adverse human health or plant damage effects might be anticipated. Modelling studies have been able to account for many of the features observed in these photochemical episodes including the formation of ozone, PAN and visibility reducing aerosols. In the Harwell study the impact of future motor vehicle emission controls on ozone concentrations in the UK was investigated using a 2 layer model integrated along a conceptual trajectory. The trajectory was located over central London at 0600hrs and advected westerly with the average diurnally varying windspeed under anticyclonic summertime conditions, reaching Bristol in the early evening. The layers consisted of a boundary layer with

diurnally varying depth and a 2nd layer which acts as a reservoir for pollutants. Emission of SO_2 ,NO, CO and 37 hydrocarbons were based on population density and includes the variation due to the diurnal cycle of motor vehicle usage. Figure 8 shows examples of the many calculations of Derwent and Hough(1986). The first 24 hours of the results were used for initialisation and should be ignored. The squares represent the O_3 concentration under present day conditions, the crosses assume no change in emission standards of vehicles while allowing for an increase in vehicle use of 54% and the diamonds show the results given an increase in vehicle use with the 'lean burn' engine. The lean burn engine reduces hydrocarbons in the exhaust but also leads to increased NO emission because of the higher operating temperature. In the troposphere ozone is in photochemical equilibrium with NO and NO_2 and the concentration is determined by the NO to NO_2 ratio mentioned in Atmospheric Chemistry lecture 8. Thus, increasing NO in the urban area temporarily decreases O_3. However, on a longer timescale organic peroxy radicals react with NO to form NO_2 which then leads to increased O_3, as discussed in Atmospheric Chemistry lecture 6. Consequently, reduction of hydrocarbons in the exhaust gases of vehicles reduces ozone pollution, or, with increased vehicle use, can keep ozone pollution episodes down to the current level. Many other assumptions were investigated by Derwent and Hough whose paper should be consulted for further information.

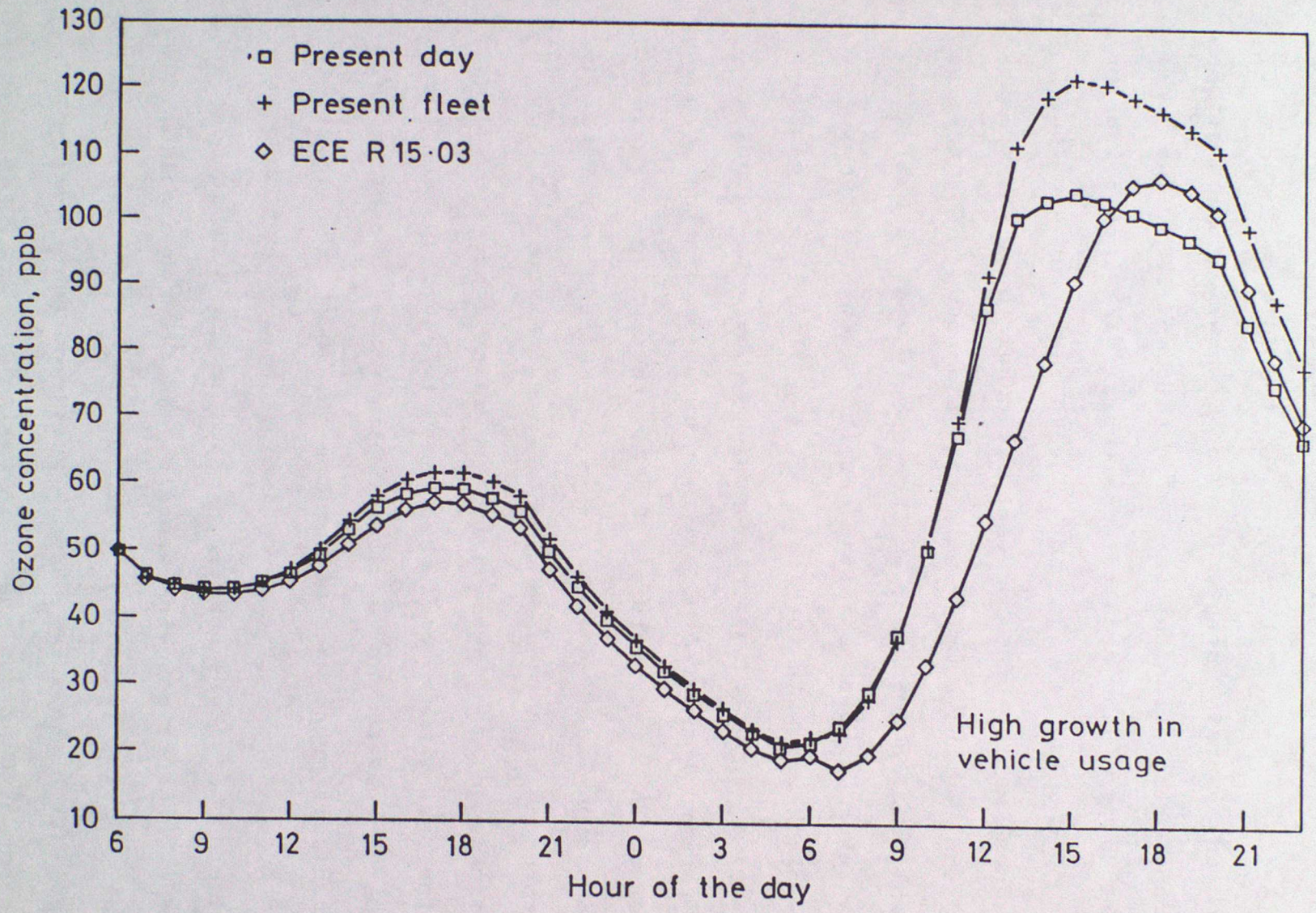


Figure 8. Ozone concentrations calculated for the present day and for the year 2000 assuming a high growth in vehicle kilometres and 1984 fleet emission factors or those for ECE R15.03. Taken from Derwent and Hough (1986).

9.5. Summary

In the last 2 lectures an attempt has been made to give a broad view of the wide range of Atmospheric Chemistry modelling studies currently in progress. All techniques have their advantages and disadvantages and careful choice of modelling technique may be required in specific cases. Ideally, several modelling methods should be applied to a given problem to provide more confidence in the calculations. To assist in this direction I finish with a table, based on personal experience, illustrating the usefulness of the modelling techniques discussed for investigating various problems relating to atmospheric chemistry.

	1-d	2-d	3-d	Trajectory
Short timescales	1	1	1	2
Long timescales	2	2	1	0
Tracers	0	1	2	0
Detailed chemistry	2	1	0	2
Detailed dynamics	0	1	2	2
Comparison with satellite data	1	2	2	2
Comparison with in-situ data	0	0	1	1

0 = poor use 1= acceptable use 2= good use

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Lecture 10: Current State and Future Directions

10.1 Introduction: Present State of Understanding of Atmospheric Chemistry

Over the course of this lecture series it should have become apparent that many aspects of atmospheric photochemistry as it relates to the present atmosphere are in general terms believed to be well understood. In part this understanding can be attributed to the availability of data from satellite borne instruments. These have provided a global observation framework in which measurements made using other techniques have been placed and with which numerical model calculations can be compared. However, this increase in understanding and observational coverage has served to highlight more clearly many areas of discrepancy. In a recent NASA document assessing the state of our understanding of the upper atmosphere many areas requiring further research were identified. Those relating to atmospheric chemistry are summarized below.

1) The magnitude of the source of reactive nitrogen from N_2O (a small proportion of the total N_2O destroyed) is uncertain. Errors in reactive nitrogen would affect all the catalytic cycles.

2) The pressure and temperature dependences of certain key hydrogen oxide reactions (e.g. $OH+CO \rightarrow CO_2+H$) are not fully understood.

3) Only an upper limit for the concentration of atmopheric BrO exists.

4) Trends in many source gases (notably CH_4) are poorly understood.

5) At present no network exists to monitor atmospheric concentrations of reactive gases.

6) Reliable measurements of OH and HO_2 do not exist in many regions of the atmosphere. Where measurements do exist, major discrepancies with theory are evident. Possible trends in tropospheric OH are not known.

7) The mechanisms by which ozone can be produced in the background troposphere are inadequately characterized.

8) The relative contributions of stratosphere/troposphere exchange and in situ production to the tropospheric ozone balance are not well known.

9) The detailed mechanism responsible for injecting H_2O into the stratosphere is not known.

10) The predicted roles of some reservoir gases in both the troposphere and stratosphere have still to be confirmed by measurements.

11) Diurnal variations of many gases involved in ozone destruction are unmeasured.

To this list could be added:

12) The importance of heterogeneous chemistry in the stratosphere (and troposphere) is not known.

This list encompasses virtually all of the aspects of photochemistry discussed in the previous lectures. Yet, improved understanding in these areas is regarded as being essential if we are to predict future atmospheric composition.

Over the next decade a number of projects are planned which collectively will address many of these problems. In this lecture, I will first describe briefly some of the techniques used to measure atmospheric composition. I will then discuss some of the planned projects and finally identify the areas the Atmospheric Chemistry Group will hopefully cover over the next few years.

10.2 Remote Scunding of Atmospheric Composition

Remote sounding instruments have been largely restricted to the measurement of stratospheric composition. Both passive and activetechniques are used. Passive devices detect either the thermal emission from, or the attenuation of solar radiation by, specific molecules in the atmosphere. Active sensors transmit radiation into the atmosphere at specific wavelengths and derive concentrations from the attenuation of the radiation which is backscattered.

Typically, resolution of passive devices would be hundreds of km in the horizontal and 2-5km in the vertical. Active devices have range (equivalently height) resolution of the order of hundreds of metres.

10.2.1 Thermal Emission Sensors

In local thermodynamic equilibrium the radiation at a particular wavelength reaching any point is determined by the atmospheric temperature structure and transmissivity. The latter is determine by the combined absorptions of the molecules at that wavelength.

Atmospheric temperature profiles are deduced from the emission from a molecule whose atmospheric distribution (and hence absorption characteristics) is known (e.g. CO_2).

For composition sounding, the atmospheric distribution is, of course, initially unknown. In this case the temperature structure is deduced first. Then, in effect, the atmospheric absorption of a gas is deduced using measurements of radiation emitted by that gas. The concentration profile is then inferred from a knowledge of the gas absorption properties. A variety of different approaches are used to provide spectral selectivity and for detection. Nevertheless, the basic approach throughout the μwave and infra-red is as given above. An advantage of thermal emission sensors is that, at least in principle, full diurnal coverage is possible, although in practice, operational constraints usually limit this.

Emission sensing can be used for a wide range of constituents which possess absorption features in the infra-red and microwave regions of the electromagnetic spectrum.

10.2.2 Solar Occultation/Backscatter Measurements

An alternative to the above is to measure attenuation in the direct solar beam as the sun rises or sets, or to detect the attenuation of scattered solar radiation. In this way the transmissions of atmospheric paths at different altitudes may be inferred, from which a concentration profile can be computed. The high solar energy means that very sensitive instruments can be used allowing, with current technology, very high spectral resolution measurements to be made. One example of such an

instrument is the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument which is a Fourier Transform Infra-Red spectrometer (FTIR) with a spectral resolution of $0.01cm^{-1}$. An example of the spectral detail visible and the selectivity possible with ATMOS is shown in Figure 1. The reliance on solar radiation and the restriction to sunrise and sunset situations precludes full diurnal measurements being obtained using this technique.

10.2.3 Active Techniques

DIfferential Absorption Lidar (DIAL) techniques have come to the fore in recent years. In all cases these have been ground or aircraft based (energy loss in the backscattered beam (the inverse square law) currently prevents their use from space). Using pulsed laser systems, radiation is transmitted into the atmosphere at two closely spaced wavelengths which have different absorptions due to the molecule under study, but which have essentially the same aerosol scattering properties. Constituent abundances are derived from the measured differential absorptions and range (or equivalently height) information is achieved by timing the return pulse. This technique has been used to measure O_3 and temperature profiles up to ≈50 km.

10.2.4 Satellite Measurements of Tropospheric Composition

The general development of sensors for the troposphere lags far behind that for meteorological instrumentation and is well behind that for stratospheric composition measurements. The technical hurdles to

obtaining space based profiles of tropospheric gases are formidable. The UV, visible and IR regions of the spectrum are more promising than the use of the microwave region because of the high sensitivity of the microwave region to pressure broadening - increasing the degree of contamination and decreasing the selectivity. The following is a list of techniques used in the troposphere from space:

Type	Examples	Species	Comments
optical filter radiometer	HIRS	H_2O	nadir viewing
gas filter	MAPS	CO	2 channel nadir viewer 2nd shuttle flight
grating spectrometer	SBUV, BUV	O_3	column only, needs sunlight
	SAGE	H_2O, O_3	upper trop. only limb scanner, occultation
FTIR	ATMOS	many	$.01cm^{-1}$ resolution 2.2-16μm, occultation

Table 1 Techniques used to measure tropospheric composition from space

The above measurements are in many cases only possible in the absence of cloud cover. Limb sounding would not be possible below cloud top height, while nadir sounding would require cloud clearing techniques to be applied.

10.3 In-Situ Techniques (Local Sampling)

Local sampling techniques enable measurements to be made on much smaller spatial scales (metres to kilometres) than are possible with remote methods. However, this highlights another problem - that of small scale variability in the measured quantities and hence possible lack of

Correlation Coefficient[a]	Altitude Interval		
	All Data	MFT	UFT
$r(O_3, CO)$	0.30	0.76	0.19
$r(O_3, NO)$	0.64	0.66	0.65
$r(O_3, T_d)$	-0.17	-0.69	-0.05[b]
r(NO, CO)	-0.06	0.32	-0.17
$r(NO, T_d)$	-0.27	-0.71	-0.04[b]
$r(CO, T_d)$	-0.14	-0.51	-0.10[b]

[a]The value r(a, b) indicates Pearson-r correlation coefficient between parameters a and b.

Table 2 Pearson-r correlation coefficients between O_3, CO, dew point and NO measurements taken during flights over the eastern and central North Pacific (Chameides et al., 1987).

representativeness. If structure is evident in the composition fields, it may not be possible to associate composition changes unambiguously with chemical transformations - advection of a concentration gradient could be wholely or partially responsible. One possible solution to this is through correlation studies. This relies on the chemical processes under investigation having similar timescales. For example, a recent study of CO related tropospheric O_3 production involving in situ measurements of CO, NO, O_3 and H_2O used a correlation method to show that high values of NO corresponded to high O_3 (Table 2). Such an approach is unlikely to be effective in all situations (e.g. in the Antarctic low stratosphere where the timescale for the O_3 depletion is likely to be long compared to possible heterogeneous chemical effects (several weeks compared to hours/days)). An alternative approach which also ocercomes the problem of different timescales is to identifyin some way an air mass as it moves in the atmosphere and evolves chemically. This approach requires a moving instrument platform and the ability to predict air mass trajectories (see below).

There is a wide range of techniques employed for local sampling, using rockets, balloons and aircraft. The different techniques have widely differing response times and sensitivities, and are subject to different interferences and contaminations. The four main categories are optical absorption, fluorescence, chemiluminescence and gas chromatography.

10.3.1 Optical Absorption

This involves measuring the absorption of an air sample at selected wavelengths, from which abundances of the absorbing gases are then inferred. The main techniques used are long path absorption (pathlengths up to 10km using a retroreflector - surface only), using dye pumped lasers as light sources. In this case the long path is necessary to provide sensitivity (e.g. for OH measurements). Alternatively, portable compact optical systems (multi-pass cells) can be used. Typically these would have 1-2m baseline lengths with total path lengths of hundreds of metres. FTIR instruments and more recently Tunable Diode Lasers (TDLs) have been used to provide spectral discrimination. For more abundant gases less sophisticated techniques are required. For tropospheric H_2O the absorption by H_2O of Lyman α radiation over a short pathlength (≈cm) is used for measurement.

Optical absorption techniques can be used for a wide range of molecules - any with sufficiently large absorptions in accessible regions of the spectrum.

10.3.2 Fluorescence

A light source (laser or other) is used to excite or dissociate molecules of the selected type. Photons associated with the radiative de-excitation of the molecule or its products are then detected. The wavelength of the radiation source and spectral filtering of the fluoresced signal provides discrimination.

This technique is highly sensitive and has been used amongst others for stratospheric H_2O, and ClO. One proposed use is for tropospheric OH measurements.

10.3.3 Chemiluminescence

Similar to fluorescence except a chemical reaction is used to produce excited molecules.

This technique has found widespread use for O_3 measurements (by reaction with ethylene) and for NO (reaction with O_3). Catalytic converters are frequently used to convert other nitrogen compounds to NO for measurement. The method is also used for NO_2 and H_2O_2 (reaction with luminol).

10.3.4 Gas Chromatography

This technique is only suitable for certain more stable molecules. It involves the passage of the air sample through a length (10s of cms) of narrow tube packed with one of a wide range of porous substances. The different times required for different molecules to pass through the column permits discrimination. Detection is by electron capture detector or flame ionisation detector. This method can be used in situ (on an aircraft) or for subsequent ground analysis of gas samples taken in flight.

Gas chromatography is used for the detection of a wide range of hydrocarbons, CFCs, N_2O and PAN.

10.4 Future Research Programs

Over the next decade several well defined measurement programs based on the above techniques will begin. A list of the more major undertakings is given below.

1) The creation of a ground based measurement network for the early detection of stratospheric composition and temperature changes.

2) Repeat flights of ATMOS.

3) The Upper Atmosphere Research Satellite (UARS)

Other possible opportunities further in the future may be free flying polar orbiting satellites associated with the proposed NASA manned space station. This project has not advanced past the preliminary design stage.

In the troposphere, there are European and American led research efforts which are designed to improve our understanding of the basic chemical cycles through field investigations, theory aided by numerical modelling and laboratory kinetics studies.

10.4.1 Early Detection Network

As it is presently planned, the network will consist of six stations of which one will be in the Southern Hemisphere. Each station will have a series of sensors based on proven technology and would measure some nine atmospheric constituents (Table 2).

The current aim is that several stations will be in place before the end of the decade.

Gas	Type	Technique
O_3	column & profile	Dobson, μwave lidar, (Umkehr)
temperature	profile	lidar
ClO	coarse profile	μwave
H_2O	profile	balloon hygrometer
aerosol	"	lidar
NO_2	column	UV/vis spectrometer
HCl	"	IR
CH_4	"	"
N_2O	coarse profile	μwave

Table 2. Summary of measurements made by the early detection network.

10.4.2 ATMOS

As indicated above, the ATMOS is an FTIR which uses solar occulation the technique to take low noise high spectral resolution absorption spectra of the atmosphere. These qualities enable a wide range of gases, many with with weak absorptions, to be detected. To date ATMOS has been flown once. Notable among the ATMOS measurements made during that flight were several gases not detected previously (including the reservoirs N_2O_5 and HNO_4) and confirmation of the presence of $ClONO_2$ in the stratosphere. It also provided the first remote measurements of the natural halocarbon CH_3Cl.

The ability of an FTIR to make *simultaneous* observations of a large number of species enhances enormously the scientific potential of the ATMOS data. For example, the fact that all the significant gases containing nitrogen oxides are measured allows not only the partitioning within the nitrogen group to be observed and compared with theory, but also enables the absolute amount to be compared with the expected source

via N_2O. While ATMOS has provided the first detection of a number of important atmospheric gases, the shortness of measurement period (≈ 1 week) and the infrequency of flights (one to date) and its limited geograhpical coverage restricts the usefulness of the ATMOS data to studies of rapid photochemistry.

10.4.3 UARS

UARS is designed to measure atmopsheric temperature, wind and the concentrations of a wide range of gases in the stratosphere and mesosphere (Figure 3). Unlike ATMOS it is designed to be launched once only and has an intended lifetime of 18 months. With a launch late in the year as currently planned it will give coverage of two Northern winters. UARS also differs from its predecessor (Nimbus 7) in that firstly the concentrations of a much wider range of gases will be measured, many by several instruments using different techniques. Secondly, The UARS orbit will precess once every ≈70 days (that of Nimbus 7 was sun-synchronous). This will allow the the emission sensing instruments to observe a complete diurnal cycle every ≈35 days. The penalty paid for this is that the UARS orbit is much nearer the equatorial plane than that of Nimbus 7. This resticts the latitude coverage to either 80°N-34°S or 34°N-80°S, depending on the spacecraft orientation.

The range of nitrogen oxide measurements (all except HNO_4 and NO_3), and chlorine measurements (HCl, ClO, $ClONO_2$ and the principal sources CFC-11 and CFC-12) will allow much more stringent tests of the most

important ozone destruction mechanisms in the middle stratosphere than possible hitherto.

From a chemical viewpoint, the main limitations of the proposed UARS data are the absence of measurements of the important radical species CH, HO_2 and $O(^3P)$.

The current launch date for UARS is late 1991.-

10.5 Future Office Research in Atmospheric Chemistry

The basis for much of the research within the atmospheric chemistry group over the next years is the Lagrangian technique outlined in lecture 9. In this technique isentropic air mass trajectories are computed either using gradient wind assumptions or directly from numerical forecast model velocity fields. Composition measurements made coincident with these trajectories (in the stratosphere largely by satellite, in the troposphere by instrumented aircraft) are then used to compute any chemical changes. Photochemical models are then integrated forward in time using the computed trajectories as boundary conditions and the model predictions tested against the observations.

10.5.1 Stratospheric Research

This will rely heavily on UARS data. With more than 16 gases measured including several chlorine species, UARS data will allow many of the initialization problems encountered in earlier work (which used 6 species from the SAMS and LIMS instruments) to be reduced. One limitation of the proposed UARS measurements is that neither OH nor HO_2

will be observed. However, the wide range of species measured and the ability to observe diurnal changes will enable much more constrained tests of stratospheric photochemistry to be performed.

In parallel with these Lagrangian studies this there will be a number of Eulerian studies in which gases with simple photochemistry (e.g. N_2O) will be introduced into a three dimensional dynamical model. This will permit the study of tracer evolution both on a seasonal timescale and during shorter dynamically active periods (e.g. sudden warmings). Depending on the success achieved, more sophisticated chemistry could then be incorporated.

The group is also involved with studies of the Antarctic O_3 depletion seen in recent years. This subject will be a major component of the group's research over the next year.

10.5.2 Tropospheric Research

The mainstay of this research is the Meteorological Research Flight C130. In past years the group has obtained gas chromatographic techniques to measure CFCs and PAN (both in situ) and hydrocarbons and nitrous oxide (by bottle sample). Measurements of O_3 and H_2O are made routinely on the C130, and work on a fast response fluorescence H_2O detector is almost complete. Collaboration with scientists at KFA Julich and at the University of East Anglia will mean the introduction over the next 12 months of detectors for NO, total reactive nitrogen, CO and H_2O_2. Other avenues under investigation are TDL systems (which would be suitable for the detection of a wide range of molecules) and a laser magnetic resonance technique for both OH and HO_2. The latter technique

is used routinely in the laboratory but using current techniques there would be a major decrease in sensitivity for operation at tropospheric pressures. Other components of this work are the developments of a means of obtaining forecasts of air parcel trajectories in the troposphere from a remote site and of a chemical model for the troposphere.

An essential requirement of the trajectory approach is that the air mass under study does not disperse rapidly. In the troposphere, the convection free centres of large slow moving anticyclones would be well suited and the intention is to make measurements which will test aspects of tropospheric O_3 photochemistry in the Azores anticyclone. Several measurement campaigns in the Azores anticyclone are anticipated over the next few years.

Other areas under study, given suitable meteorological conditions, are the roles of thunderstorms as sources of NO in the troposphere and the importance of of stratosphere/troposphere exchange in the tropospheric O_3 balance.

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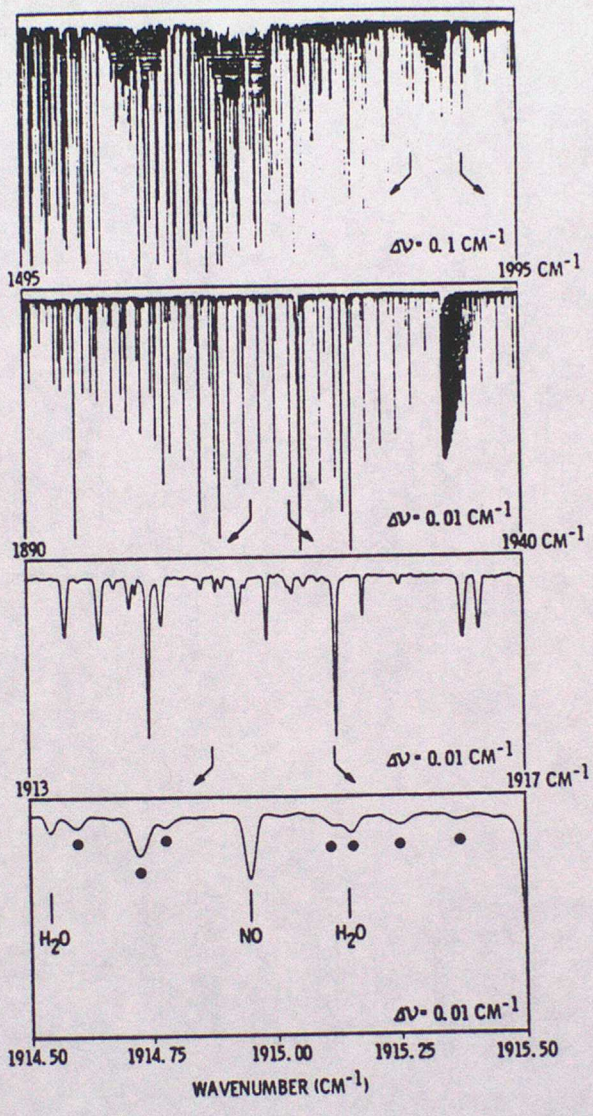

Figure 1 A spectrum taken from ATMOS. The top trace shows a 500cm^{-1} region between 1495 and 1995 cm^{-1}. The remaining three show successively narrower regions of the same spectrum ultimately displaying the region between 1914.5 and 1915.5 cm^{-1} which is used for NO detection.

Figure 2 Summary of species detected in ATMOS spectra. The bars indicate the range of useful measurements.

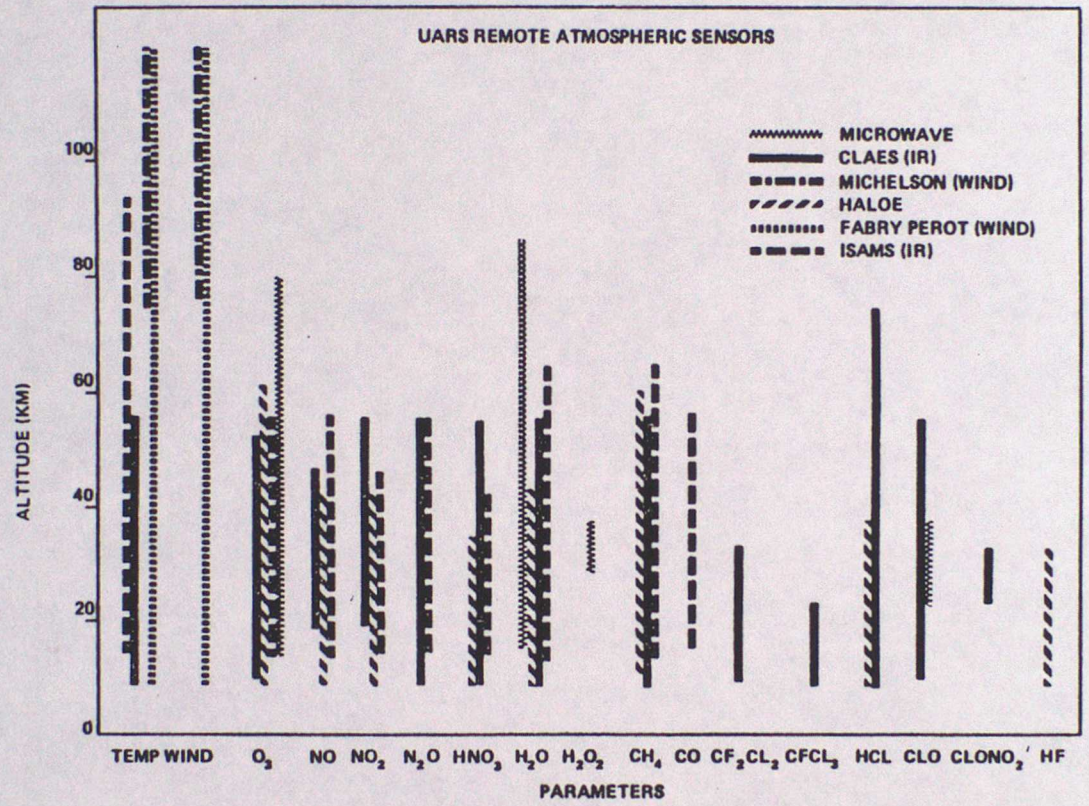

Figure 3 As Figure 3 except for the UARS satellite. Some measurements, e.g. that of N_2O_5 by ISAMS are not included.